AGRONOMIC AND ENVIRONMENTAL EFFECTS OF PHOSPHORUS FERTILIZER APPLICATION METHODS

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Saskatoon

By

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ABSTRACT

As farm size increases on the Canadian prairies, improving operational efficiency is important for growers. While seed row placement is generally considered the most effective phosphorus (P) placement method for small grains, there are few recent studies comparing agronomic effectiveness of different P fertilizer placement strategies on the prairies in modern no-till cropping systems and environmental considerations must be made in tandem as snowmelt runoff is an important exporter of P in the prairies. The objective of this research was to evaluate the effect of application strategy of monoammonium phosphate fertilizer (MAP) on crop response and P export in a simulated snowmelt runoff and leachate water over two consecutive years of application. The field study was conducted on a typical no-till field with good inherent P fertility located in the Brown soil zone in south-central Saskatchewan near Central Butte. Three in-soil MAP placement treatments (seed placed, deep banded, and broadcast with incorporation) at 20 kg P_2O_5 ha^{-1} and three broadcast (20, 40, and 80 kg P_2O_5 ha^{-1}) treatments were applied each spring along with a control without P fertilizer in an RCBD set up on two sites in the field. Wheat (*Triticum aestivum* var. Waskada) was seeded in 2015 and canola (*Brassica napus* var. LL 250) was seeded in 2016. Treatment was not significant in 2015. In 2016, treatment was significant and uptake of P by canola was significantly higher in the 80 kg P_2O_5 ha^{-1} broadcast treatment than in other treatments. In the fall of 2016 after harvest, soil monoliths were collected and used to assess vertical and horizontal distribution patterns of soil available P in the surface soil profile. Mapping of residual P indicated zones of depletion below 5-cm in the in-soil P placement treatments, likely due to stimulated root growth, while the broadcast treatment revealed minor surface loading of P. Only the broadcast application at the high rate (80 kg P_2O_5 ha^{-1}) showed enhanced export in the simulated snowmelt runoff and leachate, and a higher proportion of the P in snowmelt runoff was in the dissolved reactive fraction in this treatment. Assessment of P forms in the runoff using NMR spectroscopy suggested that higher application rates may also be associated with increased microbial activity and production of organic P forms in the soil. Due to high inherent fertility, lower rates of P would be advisable in these soils as crop response to fertilization was limited and high rates of broadcast MAP substantially increased P export in water.

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DEDICATION

I gratefully dedicate this work to my parents, Tim and LaVonne, who never stopped supporting me in obtaining higher education and always were willing to provide an ear and a coffee, and their forebears, who left in search of a home to provide a better life for their children.

I would also like to dedicate this work to the community of Herschel. It is said it takes a village to raise a child, and this is no exception.

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LIST OF ABBREVIATIONS

Acid equivalent	a.e.
Active ingredient	a.i.
Adenosine triphosphate	ATP
Aluminum	Al
Alpha-glycerol phosphate	α-glyc
Analysis of variance	ANOVA
Best management practice	BMP
Beta-glycerol phosphate	β-glyc
Broadcast and Incorporate	B/I
Broadcast at x kg P_2O_5 ha^{-1}	B(x)
Calcium	Ca
Carbon	C
Carbon dioxide	CO_2
chiro-inositol hexakisphosphate	*chir*IHP
Deep band	*DB*
Degradation coefficient	Deg
Deionized	DI
Deoxyribonucleic acid	DNA
Deuterium oxide	D_2O
Diammonium phosphate	DAP
Dissolved reactive phosphorus	DRP
Dissolved unreactive phosphorus	DURP
Electrical conductivity	EC
Ethylenediaminetetraacetic acid	EDTA
Free induction decay	FID
Glucose-6 phosphate	G6P
Hydrochloric acid	HCl
Hydrogen peroxide	H_2O_2
Inorganic phosphorus	P_i
Inositol hexakisphosphate	IHP
Iron	Fe
Magnesium	Mg
Manganese	Mn
Modified Kelowna	KM
Molar	M
Monoammonium phosphate	MAP
myo-inositol hexakisphosphate	*myo*IHP
neo-inositol hexakisphosphate	*neo*IHP
Nuclear magnetic resonance	NMR
Nucleotides	Nucl

Organic phosphorus	P_o
Orthophosphate	Ortho
Oxygen	O_2
Phosphonate	Phon
Phosphate	PO_4^{3-}
Phosphatidylcholine	Pchol
Phosphite	PO_3
Phosphorus	P
Polyvinyl chloride	PVC
Pyrophosphate	Pyro
Saskatchewan	SK
scyllo-inositol hexakisphosphate	*scyl*IHP
Sodium bicarbonate	$NaHCO_3$
Seed placed	SP
Sodium hydroxide	NaOH
Sulfuric acid	H_2SO_4
Total phosphorus	P_t
United States of America	USA
X-ray absorption spectroscopy	XAS

1. INTRODUCTION

1.1 Farm management and P fertility considerations

The number of farming operations in Canada has decreased in the past 25 years, from 280 043 operations in 1991 to 205 730 operations in 2011, with the average farm size increasing along with average operator age (Statistics Canada, 2015). To address the need to cover larger areas of land efficiently during the short and busy growing season on the prairies, larger equipment is being used, but even this machinery investment cannot account for unexpected weather interference. Due to snow and rain in the fall of 2016, only 89% of the crop was harvested in the west-central region and 91% in the northwest region of Saskatchewan (Government of Saskatchewan, 2016a). These adverse weather scenarios are not only challenging financially, but also interfere with future crop planning and preparation as precious time in spring is used harvesting the previous years' crop. Therefore, many farmers face considerable pressure to get all the seeding and fertilizing done in a very short time frame in spring on the Canadian prairies. This has led some farm operations, particularly large operations that experience difficulty in securing farm labor, to look at the operational efficiency of their spring field work.

In terms of increasing operational efficiency in spring, broadcasting of fertilizer is looked to as a possible means of speeding up the fertilizer application process. Over one thousand acres a day can easily be broadcast fertilized with a high-speed flotation applicator. However, in annual small grains production to achieve the best crop response to P (phosphorus) fertilization in the year of application, the recommended practice on the prairies is to place P fertilizer in the soil at the time of seeding in or close by the seed row to maximize early season availability as well as provide early season vigor, or a "pop-up" effect (Government of Saskatchewan, 2016b). This effect is most pronounced in low P testing soils under conditions (e.g. cold, very wet or dry) that restrict root growth and P diffusion. The gain in operational efficiency from not applying fertilizer at time of seeding comes from reduced seed tank usage in the air drill, reducing time spent refilling. This can be accomplished through pre-plant banding, broadcasting, or broadcasting and incorporating through tillage. As changes to placement are contemplated, application rate must also be considered to account for early season availability.

Broadcasting in particular may be considered an inferior placement practice for phosphorus as it leaves the fertilizer P "hung-up" in the surface soil, too far away from roots to be readily accessed, and leaving the P vulnerable to removal with water moving across the soil surface (Havlin et al., 2014). This is of concern as P runoff from agricultural fields accounts for 15% of the P entering the Lake Winnipeg drainage basin, and ultimately the lake (Lake Winnipeg Stewardship Board, 2006), with serious implications for eutrophication.

The balance between P addition as fertilizer and P removal by crops is an important consideration when examining depletion, maintenance or build-up of soil P levels and fertility. As blanket applications of the same P rates year after year are utilized, residual soil P levels end up being enriched in years with poor growth or when crops with low P demand are grown, and conversely depleted in years with high yield or crops with high P demand. Depletion is exacerbated when crops are grown with low seed placed P tolerance such as peas, flax, or canola and when low rates of seed-placed or no P fertilizer is used. Replacement of P exported in crop removal and reduction or elimination of P lost through water, wind and tillage erosion is important in maintaining P fertility of soils. Therefore, management history, including rates of P fertilizer addition in relation to crop removal, tillage practice, and rotation will all influence P fertility (Havlin et al., 2014) and the response of crops, soil and water to placement and rate of P fertilizer application. This thesis work examines crop, soil and water response to P fertilizer application strategy in a well-managed, high P fertility soil in south-central Saskatchewan.

1.2 The effect of P on water quality

Eutrophication is the nutrient enrichment of water bodies. Phosphorus imports are a primary concern in the eutrophication in lakes. In some regions, agriculture has become a major contributor as point sources of P such as urban sewage discharges become better regulated. Phosphorus is removed from fields in which excess rain and snowmelt water runs off the fields into rivers, lakes, and streams. These additions are classified as non-point inputs (i.e. not directly entering the waterway) and can account for over 90% of P inputs into eutrophied water bodies in some regions (Newman, 1995). Increased concentrations of bioavailable phosphate in this water triggers algal growth, a common symptom of eutrophication. Cyanobacterial growth in freshwaters has long been observed to cause a variety of problems, especially the development of an anoxic zone below the blooms (Kotak et al., 1993; McComb and Davis, 1993). These

conditions lead to the death of flora and fauna, reducing system biodiversity and creating foul odors and unpalatable water (Kotak et al., 1994). Algal blooms also produce trihalomethane (a known carcinogen) precursors, which produce trihalomethane under chlorination during water treatment (Palmstrom et al., 1988). While P is not directly toxic, it is apparent that the water conditions caused by P addition can be hazardous to human and animal health (Amdur et al., 1991). Therefore, it is important to understand both the nature and quantity of P exported in runoff and leachate from agricultural soils.

1.3 Characterization of P in soils and runoff

Our understanding of soil P chemistry and its characterization is still evolving, even though common methods of soil P assessment are decades old. The characterization of P has typically emphasized the "bioavailable" fraction, and bioavailable or "soil test" P is typically indexed to uptake and yield response based on field fertilizer trials. This is still commonly done today with bioavailable P assessments used for both agronomic and environmental purposes. Criteria for an effective P assessment tool as defined by Tiessen and Moir (2008) are: simple enough to be routine, extracts a measurable amount of P, have at least some plant available P, and not extract large amounts of non-plant available P. Extractions such as Olsen (Olsen et al., 1954), modified Kelowna (Qian et al., 1994), and water extraction (Schoenau and Huang, 1991) have been correlated with plant uptake to serve as basis for fertilizer recommendations and also serve as indicators of runoff potential (Stumborg and Schoenau 2008). Extractions also have some value as gauges to characterize adsorption strength based on differences in strength of extractant. In addition, correlating these extractions to amounts of P lost in leaching events or runoff can provide a simple means for assessing runoff P risk, similar to that conducted by Pote et al. (1996), Little et al. (2007), and Salvano et al. (2009).

Sequential extractions remove P in phases from a soil by applying progressively stronger extractants. The idea was first proposed by Chang and Jackson (1957) and has since been modified (e.g. Hedley et al. 1982; Tiessen and Moir, 2008). The extraction typically starts with water extractable or resin membrane exchangeable P. The soil is then extracted with a weak base (e.g. $NaHCO_3$), followed by a strong base (e.g. NaOH) and acid (HCl), with inorganic (P_i) and organic (P_o) P concentrations in each fraction often reported. Both P_i and P_o are determined using Murphy Riley (1962) colorimetry and an ammonium persulfate digest on the extracted sample to

release molybdate unreactive P to create total P. Organic P is therefore defined as total minus reactive. Therefore, some error is expected with this technique as P_o is not directly measured. Alone this technique may not be particularly useful, especially when looking at effects of P management over only a few months or years. However, this technique may be useful when applied in conjunction with other chemical and spectroscopic measurements of P, allowing insight into the nature of P as related to its extractability and nature.

In addition to extractable P, spectroscopic techniques can be applied to assess soil P status. The technique of ^{31}P nuclear magnetic resonance (NMR) spectroscopy can be used to characterize specific P compounds due to the amount of shielding the P atom receives from surrounding atoms in the compound, creating changes in the decay from a higher energy state induced by a radio frequency pulse, which in turn creates distinct peaks when Fourier transformed. These peaks can be used to determine inorganic and organic P compounds in the sample with precision, but is more useful for characterization of P_o, as many different compounds can be identified (Cade-Menun, 2005). This technique can be quantitative if the signal is of a high enough quality, or can simply be used qualitatively. While very useful in certain situations,^{31}P NMR is not a universally applicable technique due to the challenges of magnetic identification that are covered later in the literature review.

1.4 Justification of research

Phosphorus placement is currently relevant and of interest to Saskatchewan producers (Booker, 2017). In particular, producers are interested in the agronomic efficacy of alternative placement methods to in-soil, including broadcast and foliar application improve operational efficiency. However, practices that lead to accumulation of the P on the surface are liable to increase the amount of P in runoff which is a concern environmentally. While the Saskatchewan river system is not as important as the Red river is to P loading in Lake Winnipeg, it is still a significant contributor of P (Environment and Climate Change Canada, 2016). The general, consensus in the literature from North America is that in-soil placement of fertilizer (e.g. banding, seed row) is favoured over broadcasting from a crop response standpoint. Research in reduced tillage systems suggests that banding P fertilizer leads to more adsorbed P and greater availability to roots as compared to broadcasting which resulting in a higher proportion of less soluble precipitated Ca and Fe bound P (Khatiwada et al., 2012). In terms of potential

environmental impact, Gildow et al. (2016) found that banding fertilizer reduced soluble reactive P runoff by 42% compared to the baseline in Ohio. Nkebiwe et al. (2016) reported increased yield and above-ground crop nutrient concentration associated with increasing depth of fertilizer placement in the soil in a meta-analysis. However, despite the common agreement that placement influences crop P uptake and runoff, data is limited for calcareous soils typical of Saskatchewan. On a Brown Chernozem with history of cereal-tillage fallow rotation, little or no P fertilization, and low levels of plant available P, Weiseth (2015) found a benefit to in-soil placement compared to broadcast for soybean in Saskatchewan both in crop yield and reducing P in snowmelt runoff, but did not conduct studies on other crops. Mooleki et al. (2010) reported differences in crop response relating to placement of P bands in Saskatchewan, but did not have a broadcasting treatment for comparison, nor was the nature of residual soil P and potential for export off site in water examined. Therefore, there is an apparent gap in knowledge, not only in regards to the efficacy of P fertilizer in prairie soils as affected by placement and rate, but also on the nature and quantity of P potentially exported in snowmelt runoff and leaching water.

1.5 Hypothesis and objectives

Considering the lack of information in Saskatchewan regarding fertilizer P placement and its relationship to nature of residual soil P and P in runoff and leachate, the following objectives for this thesis research were established:

i) To assess the effect of P fertilizer application strategies (seed row placed, deep banded, broadcast and incorporated, broadcast) on wheat and canola yield, P fertilizer uptake, and recovery at two locations in a well-managed, high P fertility field in south-central Saskatchewan. The agronomic effectiveness of foliar applied P versus seed placed P was also assessed at two other low P fertility locations and is covered in the appendix.

ii) To determine the nature and fate of residual fertilizer P in soil and its potential contribution to P export in water by assessing amount and speciation of P in soils and simulated snowmelt runoff and leaching water collected from the P placement treatments. This is accomplished through use of various labile soil P assessment techniques, a sequential extraction to reveal chemically separable P fractions in the

soil, and ^{31}P NMR spectroscopic techniques to examine the content and nature of P exported in runoff and leachate water.

The objectives are intended to address the following general hypotheses put forward for this thesis research:

i) In-soil placement of fertilizer P will improve yield and P uptake as compared to surface broadcast alone as placement proximity is important for early access due to its immobility. The effect will depend on crop, environmental conditions and other management factors related to P fertility such as application rates.

ii) Placement of fertilizer P will be a significant factor affecting the distribution of residual available P found in the soil post-harvest due to its low mobility.

iii) In-soil placement and lower rates of P fertilizer additions will result in lower amounts and proportion of P in soluble forms, and lower runoff and leachate export as compared to surface applied P fertilizer treatments at high rates as these are likely influenced by contact with melt water.

1.6 Structure of thesis

The structure of this thesis includes separate main chapters covering the research intended for publication. Therefore, the first chapter provides the overall thesis introduction and justification for the research. Chapter 2 is a review of relevant literature with emphasis on soil and water P chemistry and its assessment. Chapter 3 is the first research chapter and addresses the agronomic effects (crop yield, P uptake, recovery) as affected by P fertilizer treatment. Chapter 4 is the second research chapter addressing the fate of the added P fertilizer after two growing seasons, including the nature and distribution of residual P in the soil post-harvest, and the nature of P in simulated snowmelt runoff water and leachate, with an emphasis on assessing environmental risk. Chapter 5 is a synthesis of the research, addressing the broader impacts of the findings, along with conclusions and suggestions for further research. Chapter 6 contains literature cited in this thesis. Information on foliar P trials, which were an ancillary component of the work, as well as ANOVA tables and details on outlier removal are provided in the appendix.

2. LITERATURE REVIEW

2.1 Phosphorus in soil and water

2.1.1 Soil phosphorus speciation and cycling

Phosphorus exists primarily in the soil solution as orthophosphate, with the orthophosphate form dependant on its pH as it behaves as a weak Lewis base (Fig. 2.1). As phosphoric acid is triprotonated, it has three pK_as: 2.12, 7.21, and 12.67, each representing 50% dissociation of a proton at a given pH. Therefore, over typically encountered pH range of 4 to 10, phosphate in soil solution is mono- or diprotonated orthophosphate. P differs from NO_3^- and SO_4^{2-} due to its low solubility and high reactivity in the aqueous phase. This alters how P soil levels are managed compared to N and S.

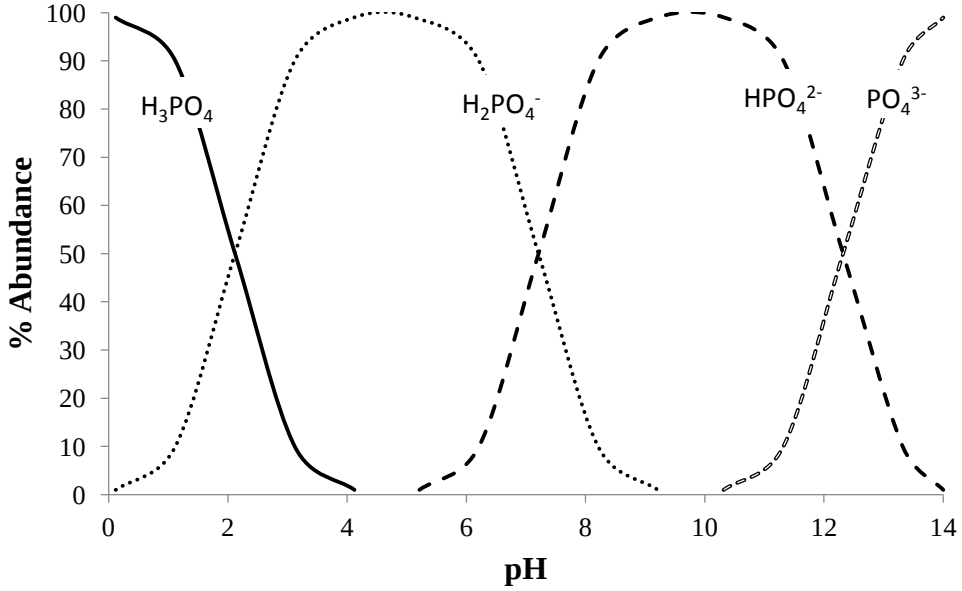


Figure 2.1: Speciation of orthophosphate as influenced by pH.

Orthophosphate in soil solution is the immediately plant available form of P (Ullrich-Eberius et al., 1984; Schachtman et al., 1998). Orthophosphate is particularly reactive in soils, with a large proportion of added orthophosphate becoming adsorbed and/or incorporated into mineral surfaces through ligand exchange (Pearson, 1963) or undergoing precipitation. Precipitation occurs through reaction with Fe and Al in acidic pH conditions, and to a larger extent with Ca and Mg in neutral to alkaline soil pH conditions (Havlin et al., 2014). As most soils in Saskatchewan are calcareous in nature, Ca and Mg precipitation reactions are likely more

dominant in these systems, as both Mg^{2+} and Ca^{2+} are hard acids and PO_4^{3-} is a hard base (Lemire et al., 2013). Stable Ca (e.g. $Ca_{10}(PO_4)_6(OH, F, Cl)_2$) and Mg precipitates and minerals are thought to be the main source of occluded P in these soils, although Mg is generally less important than Ca. On the other hand, in highly weathered, acidic soils, strengite ($FePO_4*2H_2O$), vivianite ($Fe^{2+}\ Fe_2^{2+}(PO_4)_2*8H_2O$), variscite ($AlPO_4*2H_2O$), and other Fe and Al phosphates are the main occluded P forms (Hinsinger, 2001).

In soils that are older and more highly weathered than those in Saskatchewan, differing stable pools of P form. Parton et al. (2005) modelled the changes in distribution of soil P among different forms during soil formation and showed that between 10 000 and 100 000 years, occluded and organic P (P_o) forms start to become the main pools of P over the primary minerals and labile inorganic P (P_i). Over time, P in solution derived from weathering, mineralization and fertilization progressively enters into stable pools through precipitation, adsorption, and humification, that reduces the available fraction. Due to natural weathering or N fertilizer application, pH is reduced (Riley and Barber, 1971), dissolving and releasing the metals that can form PO_4 precipitates.

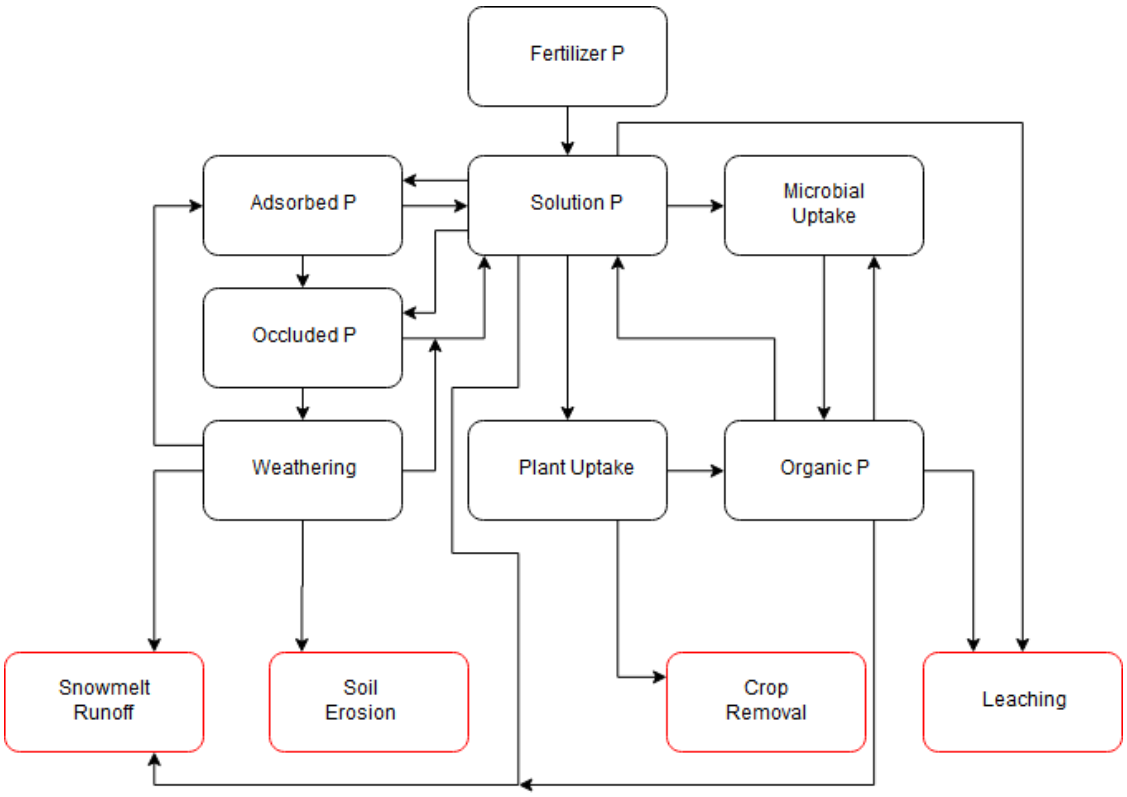


Figure 2.2: Conceptual diagram of P cycling in agricultural ecosystems. Red boxes indicate processes of removal.

A schematic depiction of P cycling in agricultural soil-plant systems, identifying different pools of soil P and inputs and outputs, is shown in Figure 2.2. Phosphorus fertilizer addition as input, and crop removal of P as output, are the dominant drivers of P status of soils. Moreover, soil solution P is generally not naturally replenished fast enough from the solid phase pools at the root surface so depletion of P in the rhizosphere drives diffusion (Hinsinger, 2001), which is the primary mode of transport for P to move to root surfaces (Barber, 1995). Solubilization of occluded P forms by plant roots and microorganisms in the rhizosphere is an important mechanism for mobilizing P in the soil environment.

Balance must be achieved through management in the relation between P inputs and outputs to prevent excess P accumulation or depletion. Since P is generally translocated by the plant to reproductive organs, much P is removed with the crop at harvest. Appropriate P additions to maintain balance over time can be calculated using predicted crop grain P concentrations and yield (P removed) over a number of years.

Alterations of rhizosphere pH are used by many plants to improve short-term bioavailability of P in soils of low labile P content, as demonstrated by Riley and Barber (1971). Some crops demonstrate an ability to acidify the rhizosphere such as legumes (Aguilar and Diest, 1981; Neumann and Romheld, 1999), wheat and tomato, (Neumann and Romheld, 1999) and rape (Bekele et al., 1983) through increased cation uptake as well as exuding organic ligands (Jones and Brassington, 1998). Additionally, bicarbonate can be an effective displacer of phosphate (Nagarajah et al., 1968; Kafkafi et al., 1988), particularly in calcareous soils and in the rhizosphere, where microbial activity will increase CO_2 concentration (Gollany et al., 1993; Hinsinger, 2001). Plant production of extracellular, compound specific phosphatases allows for organic P compounds in the rhizosphere to be rendered available through enzymatic release of phosphate (Richardson et al., 2005).

2.1.2 Water P speciation and cycling

Soils can make significant contribution to P in water bodies such as streams, rivers and lakes. Non-point sources from agricultural lands is P input from diffuse indirect sources in the watershed, such as runoff, leaching waters and wind-blown soil deposition (Novotny and Olem, 1994). In some instances, these can be the main inputs of P. For example, non-point sources were identified as responsible for greater than 90% of P in one third of rivers and streams in the USA

according to Newman (1995) and Carpenter et al. (1998), with rain being the driving force (Turner, 2005). However, on the prairies it is largely transport from soils to water bodies via snowmelt runoff water that is the major process (Lake Winnipeg Stewardship Board, 2006) and that is therefore emphasized in this thesis. Runoff P in the Canadian prairies is of concern due to the entry into water of immediately bioavailable forms like orthophosphate ions (dissolved reactive P_i), soluble P_o that can be rapidly mineralized, as well as solid phase P_i and P_o forms (particulates) that will slowly release orthophosphate to the water over time.

The P in runoff water can be operationally defined into three categories: dissolved reactive phosphorus (DRP), dissolved unreactive phosphorus (DURP), and particulate phosphorus. Dissolved P is operationally defined in this thesis as that which can pass through a 0.45-µm filter paper, and particulate phosphorus is the remaining fraction. It is important to note that dissolved P will include that sorbed to colloids, but is used for analytical convenience. The separation involves filtering the water and determining molybdate reactive P using colorimetry. Dissolved reactive P in the filtered solution is determined directly by applying ammonium molybdate/ascorbic acid colorimetry (Murphy and Riley, 1962) to the filtered extract. This DRP is inorganic orthophosphate. Digestion of the solution, commonly with an ammonium persulfate digestion (Tiessen and Moir, 2008), provides measurement of total (inorganic and organic) P. The difference between total P measured in the filtered solution by ammonium persulfate digest and the P_i is used to provide a value for DURP. The role of DURP is still poorly understood. For example, Ekholm (1994) found that DURP was not bioavailable in an algal assay, but the understanding of the nature of DURP was incomplete at the time. DURP constitutes dissolved P_o and colloidal P. While DURP can buffer bioavailable P through enzymatic hydrolysis, the nature of the compound affects the kinetics (Table 2.1).

Understanding nature of microbial assimilation and use of P in soils and water is important. Microorganisms comprise a small percentage of total P in soils, with concentrations of microbial biomass P ranging from 4.4-77.2 mg P kg^{-1} (Oberson et al., 1999; Ross et al., 1999; Chen et al., 2000; Schärer, 2003; Turner et al., 2001; He et al., 1997) depending on soil location and management. While microbes preferentially use inorganic orthophosphate as P sources, they are the main user of P_o compounds, using them either intact or through enzymatic hydrolysis to orthophosphate (Table 2.1). Thus, they are a main driver of P_o turnover in soils. Organic P can also be assimilated through traffic ATPase, a transporter that derives energy from the hydrolysis

of ATP, resulting in free P_i. Symports and anti-ports are also used as methods of direct P_o uptake coupled to proton gradients or are ionically driven (Maloney et al., 1984). Furthermore, microbes can access reduced PO_3 (Naudin et al., 2001) that higher plants cannot, illustrating that microbes are invaluable in cycling plant unavailable P. Enzymatic hydrolysis can release phosphate from organically bound P from glucose 6-phosphate, glycerol 3-phosphate, adenosine bases, pyro- and polyphosphate, and other monoesters (Heath, 2005). Diesters are not available to this enzyme. Additionally, enzymatic activity is suppressed by free PO_4 and arsenate, requiring depletion of PO_4 through biological assimilation before more is released. Inorganic PO_4 is more important as an direct contributor to eutrophication than P_o, but hydrolysable P_o compounds do play a role as they buffer or maintain the orthophosphate concentration when depleted. Colorimetric analysis does not measure P_o but only free PO_4^{3-} ions (Murphy and Riley, 1962) and there is no consistent agreement on the proportion of P_o in the literature (Turner, 2005). Therefore, analysis of DRP without also measuring P_t does not provide a complete depiction of bioavailable P in runoff. For this reason, ammonium persulfate digestions are commonly conducted (Tiessen and Moir, 2008). An in-depth review of microbial P use is out of the scope of this chapter and can be found in Oberson and Joner (2005).

Table 2.1: Uptake of organic P compounds by *Escherichia coli*. Adapted from Heath (2005). ATPase=adenosine 5'-triphosphatease, Pst=phosphate specific transporter.

Substance	Action	Process	Catabolic repression
Phosphate	Uptake of phosphate	H^+-symport, Traffic ATPase	-, No
Phosphate monoesters, pyrophosphate, tripolyphosphate	Hydrolyse phosphate monoesters	Uptake of phosphate by Pst	No
5'-mononucleotides, 3'-mononucleotides, 2',3'-cyclic nucleotides	Hydrolyse nucleotides	Uptake of nucleotides by specific transporters	No
Phosphonates	Uptake of intact dissolved organic phosphorus	Traffic ATPase?	No

Table 2.1 cont.

Glycerol, glycerol 3-phosphate	Uptake of intact dissolved organic phosphorus	H^+-symport or phosphate-antiport	Yes
Glucose 6-phosphate, hexose phosphates, glycerol 3-phosphate	Uptake of intact dissolved organic phosphorus	Phosphate-antiport	Yes

Bioavailable phosphate in water contributes to algal blooms and eutrophication. Eutrophication is undesirable as it detracts from utilization of water for recreation purposes, for example in the eutrophic Gippsland Lakes in Victoria, Australia (EPA, 1995), and because it induces hypoxia and creates toxic compounds (Amdur et al., 1991; Kotak et al., 1994). Smith (1998) summarized the adverse effects of eutrophication: increased phytoplankton biomass, toxic phytoplankton community build-up, increases in gelatinous zooplankton, increased biomass of benthic and epiphytic algae, macrophyte species composition change, coral reef death, increase in water opacity, water treatment problems, O_2 depletion, increased fish kill, and reduced water aesthetics. Therefore, practices need to be taken to reduce non-point P inputs from soils to water in order to slowly return these water bodies to natural P concentrations (e.g. Lemunyon and Gilbert, 1993; Sharpley et al., 2003; Bechmann et al., 2007; Tiessen et al., 2010).

2.2 Management, phosphorus mobility, and water quality

The dominant P fraction exported in water is variable, difficult to predict, and dependent on location (environment) and management as shown in Table 2.2. Predictably, fertilized treatments tended to result in a greater proportion of DRP while manured treatments usually resulted in a greater fraction of DURP (e.g. Ashjaei et al., 2010), consistent with comparisons reported in Kleinman et al. (2002). However, other factors play a role in influencing the nature of runoff P. For example, live vegetation in runoff areas increases nutrient concentrations in runoff water compared to crop stubble (Elliott, 2013). Land use also appears to influence the nature of the P in the runoff (Heathwaite and Jones, 1996).

Organic P forms in runoff water are variable. P monoesters make up most of the P_o, despite diesters being the dominant contributor to soil P_o pools (Turner, 2005). These monoesters

occur primarily as inositol phosphates, with phytic acid (*myo*-inositol hexakisphosphate) being the dominant molecule (Cade-Menun et al., 2005; Richardson et al., 2005; Turner et al., 2012). This is due to differential stabilization allowed by bearing six phosphates. Due to differences in charge density, phytic acid is sorbed tighter than other monoesters and can compete with PO_4 anions for bonding sites (Turner, 2005; Bowman et al., 1967; Anderson et al., 1974). Consequently, other monoesters are degraded into P_i faster than phytic acid and phytic acid is less mobile as an organic compound due to its stabilization through sorption. Other organic compounds that are lost in export (e.g. DNA and phospholipids), are indicators of microbial activity. Further details of the nature of export of organic P can be found in Turner (2005).

Table 2.2: Dominant fraction of P exported in water.

Location	Water	Dominant P Fraction	Treatment Type	Citation	
Southwest Australia	Runoff	DURP	Fertilizer	Sharma et al.	2017
Delaware, USA	Runoff	DURP	Manure	Toor and Sims	2016
Southwest Australia	Leachate	DURP	Fertilizer	Sharma et al.	2015
Belgium	Runoff	DRP	Land Use	Verheyen et al.	2015
Canadian Prairies	Runoff	DRP	Pasture	Cade-Menun et al.	2013
	Runoff	DURP	Cropland		
Korea	Leachate	DURP	Fertilizer	Lee et al.	2013
	Runoff	DRP	Fertilizer		
Canadian Prairies	Runoff	Dissolved	Tillage	Tiessen et al.	2010
Eastern Australia	Runoff	DRP	Fertilizer	Toor et al.	2005
	Runoff	DURP	Manure		
Southwest England	Leachate	DRP	Grassland Type	Turner and Haygarth	2000
Southwest England	Runoff	Unreactive	Land Use	Heathwaite and Jones	1996

While marked differences are apparent in water P forms and amounts when comparing the effects of manure versus mineral P fertilizer application, research is lacking on the influence of fertilizer placement and rate on the composition of P in runoff water. For example, P broadcast on the soil surface is more difficult for plants and microbes to access, which should lead to more DRP. Conversely, P (i.e. seed placed) that is more easily accessible and which promotes growth may be expected to result in more DURP considering the greater uptake efficiency.

2.3 P application strategies

2.3.1 Timing

Meeting early season plant requirements for P in annual cropping systems is an important agronomic aspect of P application in agricultural soils, as early season P stress has been shown to significantly reduce yield of annual crops in the prairies (Grant et al., 2001). When P stress is induced, concentration of P_i in plant tissue is reduced more than P_o (Ozanne, 1980) and P is mobilized from young vegetative plant parts to older plant parts. Later season supply of P can also be beneficial, as uptake of P post-anthesis by wheat was demonstrated by Miller et al. (1994). This is the basis for foliar application of fertilizer P when soil reserves are not sufficient to meet the crop need and when a "top-up" later in the season is required. Further review on foliar application can be found in Noack et al. (2011).

In general, application of fertilizer P in-soil close to or at the time of seeding of annual crops has been the prescribed timing of application on the Canadian prairies (Grant et al., 2001). It is well known that early season supply of P enhances both root and shoot growth (Brenchly, 1929; Bar-Tel et al., 1990; Schjørring and Jensén, 1984). Ability to overcome P deficiency is enabled by increased root growth. Increased concentration of P in the seed may also help overcome early season deficiency by extending the time available for the roots to search and access P before the seed reserves are depleted (Spinks and Barber, 1948).

2.3.2 Placement

Grant et al. (2001) summarized early studies conducted on P placement that generally concluded that placement of P near the seed, or in bands, was optimal. Placement of P fertilizer in the seed row or close-by as a "starter" ensures early access to P by the roots of the young seedling. The "starter" benefit is especially important when root growth is limited by adverse soil conditions such as cool temperatures, and starter P was observed to have a greater effect under conditions of low P supply by diffusion (Barber, 1958). Some recent research has reported less response of crop yield to placement of P fertilizer, perhaps because of environmental conditions or soil P status, but differences are more often reported for crop P recovery and uptake (Mckenzie et al., 2001; Holloway et al., 2001; Lu and Miller, 1993; Rehm et al., 2003; Scott et al., 2003; Lemke et al., 2009). In Saskatchewan, soil moisture appeared to have a more important effect on crop yield than P fertilizer placement (Mooleki et al., 2010). Lemke et al. (2009) and

Grant et al. (2001) both describe the influence of soil conditions during the early season, specifically in reference to temperature, which adversely affects diffusion rate. While this may be important in P availability in the first week or so after seeding, only a small amount of P is taken up from the soil at this time (Kalra and Soper, 1968). Improvement in conditions later on may compensate for early season limitations. Therefore, placing P for early season access may not always be advantageous due to good growing and soil conditions that facilitate uptake of P.

Granular P fertilizer placement strategies can be separated into two categories: in-soil (seed row, band, broadcast and incorporate) and surface (broadcast). In line with early research (e.g. Barber, 1958; Mitchell, 1957) indicating benefits of in-soil placement of P close to roots, and availability and adoption of banding seeders, has resulted in widespread use of seed, side or mid row banding of P at the time of seeding on the Canadian prairies.

Seed row banding application is placement of P fertilizer with the seed in the same furrow as the seed during seeding (Government of Saskatchewan, 2016b). Side and mid row banding involves placement of the P fertilizer one or more cm horizontally from the seed row in a separate band, usually lower than the seed row. Mid row bands are typically further from the seed row than a side band. Fertilizer P can also be placed directly below the seed row. In-soil application of P that is not in a band is less common, but can be achieved through broadcasting P followed by tillage to incorporate the P into the soil. Surface application of P is done through broadcasting without incorporation, relying on vertical movement with water and diffusion to reach the rooting zone. When surface broadcasting, the rate of application is typically adjusted upward to help ensure sufficient P reaches the rooting zone. In Saskatchewan, a recent study by Mooleki et al. (2010) documented that side banding, mid row banding, and seed row placing P were all effective placement methods.

2.4 Analytical techniques for assessing soil P status

2.4.1 Wet chemical techniques

Wet chemical techniques are useful for operationally defining the nature of soil P as determined by the strength of an extractant. These techniques are usually reliant on colorimetry for determining the concentration of P in a solution through the formation of a blue phospho-molybdate complex (Murphy and Riley, 1962), although P concentrations in extracts can also be assessed using optical emission spectroscopy. For extractants intended to assess the labile, plant

available fraction, the soil concentration may then be used to generate a fertilizer recommendation based on calibration data from fertilizer response trials that relate crop yield increase from fertilizer application rates to soil extractable P levels.

The most common extraction for labile soil P is the Olsen extraction which uses sodium bicarbonate as an adsorption site competitor to displace adsorbed P and dissolve slightly soluble precipitates (Olsen et al., 1954). At the time of development, dilute acid extractions were criticized due to secondary precipitation reactions. This can be circumvented by using an alkaline extract such as $NaHCO_3$. The high pH of the extractant (i.e. 8.5) means that the Olsen extraction will tend to overestimate P availability in acid soils, and is preferred for neutral and alkaline soils (Qian et al., 1994).

In 1988, van Lierop proposed a new extracting solution of ammonium fluoride and acetic acid for measuring available P in neutral and alkaline soils. The extraction was successful for P, but did not perform as well for K (van Lierop and Gough, 1988), which resulted in the addition of ammonium acetate to enable measurement of both available P and K in the same extract (Qian et al., 1994). Qian et al. (1994) reported that correlation with plant uptake was lower for extracted P and K in acid soils compared to neutral and alkaline, but that the test performed well enough to be used in both conditions. The authors reported that the test also correlated better with canola uptake than Olsen (Kelowna r^2=0.76*** Olsen r^2=0.67***) and suggested it be used as a substitute for the Olsen test.

Anion exchange resins are another means of assessing soil P status. Anion exchange resins in bead form have been used as a method for evaluating soil P status since the 1950s (Amer et al., 1955; Moser et al., 1959) and used to assess exchangeable available P in a number of studies (Cooke and Hislop, 1963; Saunders, 1964; Bowman et al., 1978; Sibbeson, 1977; Sibbeson, 1978; Sibbeson, 1983). More recently, the use of anion exchange resins in membrane form was developed to utilize their ability to provide a measurable surface that will adsorb P by anion exchange, thereby preventing soil solution from attaining equilibrium and resulting in release and sorption of labile P from the solid phase (Schoenau and Huang, 1991). The method relies on having a positively charged surface (e.g. primary amides) saturated with bicarbonate ions through pre-treatment with 0.5 M $NaHCO_3$. The positively charged surface adsorbs anions in the solution, such as NO_3^-, PO_4^{3-}, and SO_4^{2-} via exchange with the bicarbonate anion. The membrane with the sorbed nutrient anions from the soil is then eluted using weak acid to

displace the anions into solution, which can then be analyzed through colorimetry. The method is robust and, unlike chemical extraction, is independent of conditions like pH that will influence the relative amounts of labile P that are removed in chemical extractions.

Water extractable P is another extraction that was adopted due to its ability to provide indication of relative P availability in a variety of soils. The method was shown to be useful by Schoenau and Huang (1991), who used the method recommended by Sorn-Srivichai et al. (1988), with a wide soil:solution ratio to drive dissolution of less soluble phosphate precipitates.. Although the extracting solution (deionized water) is inexpensive, other drawbacks exist for this extraction. The main drawback is that the filtering of the extract is challenging. In this method, 0.45-µm filters are used in a vacuum filtration system, which adds to the cost and time invested. Furthermore, low levels of water-extractable P can be an issue, particularly when a wide soil:solution ratio is used, leading to analytical problems if P concentrations in the extract are below the detection limit of the instrumentation.

Many other extractions exist for P, but few fit the requirement for simplicity or are only applicable to soils with certain characteristics outside of those normally encountered in prairie soils. Mehlich-3 (ethanol, ammonium nitrate, ammonium fluoride, nitric acid, and EDTA) and Bray-1 (ammonium fluoride and hydrochloric acid) are commonly used soil P tests for labile, available P that are used with success on acidic or neutral soils (Mehlich, 1984; Bray and Kurtz, 1945). As most Saskatchewan soils are neutral to alkaline, tests developed and calibrated for acid soil conditions have limited applicability.

2.4.2 Spectroscopic techniques

Spectroscopic techniques are an appealing approach for non-destructive qualitative and quantitative analysis of P. The creation of artifacts during the assessment is reduced compared to many chemical extractions as described in the previous section. However, certain techniques appear to be better suited depending on the type of P compound that is desired to be analyzed. For example, X-ray absorption spectroscopy (XAS) appears to be better suited to differentiating P_i minerals than ^{31}P nuclear magnetic resonance spectroscopy (NMR), but ^{31}P NMR would be the preferred technique for analyzing P_o species, while attenuated total reflectance Fourier transformed infrared spectroscopy (ATR-FTIR) is an emerging technique in soil science that is useful for flow-through systems examining sorption mechanisms on mineral surfaces (Hamilton

et al., 2017; Yan et al., 2015; Parikh et al., 2014; Xu et al., 2014; Johnson et al., 2012; Guan et al., 2006; Guan et al., 2005, Giesler et al., 2005). Research using XAS to assess nature of P_i compounds in calcareous soils has shown that P commonly forms Ca phosphates and adsorbed P, with some Fe P (Liu et al., 2015; Kar et al., 2012). As this thesis work uses ^{31}P NMR spectroscopy, it will be emphasized in this review.

^{31}P NMR spectroscopy methodology can be divided into two types: solid state NMR, or solution NMR. The latter increases the signal to noise ratio and reduces collection time by concentrating the P in the sample, increasing signal quality and reducing the number of scans needed for each sample. Furthermore, solid state NMR results in low spectral resolution for a variety of reasons outlined by Cade-Menun (2005) such as chemical shift anisotropy and the presence of paramagnetic ions. ^{31}P NMR works through the natural magnetic properties of odd numbered isotopes. Odd number isotopes generate a half integer spin, creating a magnetic moment. As ^{31}P is 100% abundance in nature, it is ideal for NMR. The applied magnetic field (B_0) causes alignment of the magnetic dipole into a parallel configuration. As a radio frequency (RF) pulse is applied, the nuclei absorb the energy and are excited into an antiparallel spin. The excited spins of the nuclei generate an electrical field near the detectors, capturing the excited signal, and decay to more stable orbits through energy emission. A typical solution ^{31}P consists of an RF pulse, an acquisition period when emitted energy is collected, and then a delay period to make sure all nuclei relax back to equilibrium. This is repeated as many times as needed. The relaxation of the nuclei, either through T_1 (spin-lattice) or T_2 (spin-spin) relaxation, is measured as free induction decay (FID): intensity versus time. T_2 relaxation is more important in solid state NMR, while both are equal in solution NMR (Cade-Menun, 2005). T_1 is governed by the mobility of the lattice (higher mobility results in more interaction) and the γ (gyromagnetic ratio, a fundamental constant) of the nucleus. It is important that the pulse delay time account for all relaxation in the sample if the study requires quantitative results (Cade-Menun et al., 2002). The delay time can also be shortened if paramagnetic ions are present in the sample to increase relaxation rate (Turner et al., 2003a), but can increase line broadening (Cade-Menun et al., 2002).

Prior to analysis on the magnet, the sample must be prepared for analysis in solution NMR. Preparation involves three steps: concentration, extraction, and extract concentration. Concentration in both cases is done through lyophilization to prevent hydrolysis induced by high

temperatures (Cade-Menun, et al., 2002; Turner et al., 2003b). Extraction can be done using a variety of methods to release P_o as well as paramagnetic ions. Extractants used include NaOH, Bu_4NOH, cation exchange resin (Chelex®), fluoride, and EDTA in varying combinations with each other (Cade-Menun, 2005; Sumann et al., 1998; Cade-Menun and Preston, 1996; Condron et al., 1996; Gressel et al., 1996; Adams and Byrne, 1989; Hawkes et al., 1984; Emsley and Niazi, 1983; Newman and Tate, 1980). EDTA and Chelex are both used to dissociate P from paramagnetic ions, while the other extractants remove organic matter. After the extract is concentrated, it is redissolved immediately before analysis in the probe. While different solvents can be used, D_2O is common as it allows for the signal lock on the spectrometer (Cade-Menun, 2005). The sample can then be inserted into the magnet.

After the sample has been scanned and collected many times, the resulting data is aggregated into a single FID figure. This is Fourier transformed to ppm (Hz per MHz decay) with chemical shifts being caused due to shielding of the P nucleus by the electron clouds of other nuclei in the compound, causing interference in the transfer of energy through the electromagnetic field. For ^{31}P NMR, chemical shifts are set relative to orthophosphate in an external sample of 85% orthophosphate. Orthophosphate is commonly standardized to 6.000 ppm in the spectra after processing. More shielding (e.g. polyphosphate) show a net chemical shift to the right into the negatives whereas less shielded P compounds, such as phosphonates, are chemically shifted to the left into the positives.

The P NMR spectra can generally be divided into four areas: phosphonates (30-7 ppm), monoesters (between 7 and 2.5 ppm), diesters (between 2.5 and -3.5 ppm), and polyphosphates (between -3.5 and -30 ppm). Specific peaks can be identified in each region, but peak selection is a semi-quantitative process as both visual assessment and software selection are both used. Peak selection features appear in processing software, but are not perfect. They must be used in conjunction with experience and integral tracing features to identify differences between noise and low concentration compounds. Once peaks are selected, peak assignment can be done by comparing known peak values in the literature with those on the spectrum (e.g. Turner et al., 2003b; Makarov et al., 2002a; Makarov et al., 2002b; more summarized by Cade-Menun, 2005). Peaks can shift slightly based on experimental procedure but are generally close. If the peak overlaps with several compounds (e.g. *myo*-inositol hexakisphosphate), spiking a known

compound into the sample may be needed to accurately identify the peak, as factors such as pH can alter the chemical shift via proton dissociation.

Although solution ^{31}P NMR spectroscopy has been used since the 1980's, there is still no single established standard method for sample preparation. Differences in techniques utilized among research groups has led to a greater push for standardization of methodology (Cade-Menun, 2005). A variety of factors makes the selection of a single standard method difficult, such as low P concentrations, salt interference, and paramagnetic ion concentrations. In solution ^{31}P NMR, interference from paramagnetic ions can be a large issue, also some preparation methods may be more prone to degradation through hydrolysis (Turner et al., 2003b), and different extractants do not draw from the same pools of phosphate. Additionally, certain extractants remove paramagnetic ions, which increases the signal to noise ratio but also increases the delay time between pulses (Turner et al., 2003b). These challenges were encountered in this thesis research in the application of ^{31}P NMR spectroscopy to characterize the P compounds contained in runoff and leachate water collected, as low paramagnetic ion concentration in most dissolved extracts made quantitative analysis impossible.

3. AGRONOMIC EFFECTS OF PHOSPHORUS FERTILIZER APPLICATION STRATEGY

3.1 Preface

This chapter examines response of crops and soil to P fertilizer placement and rate treatments. Grain and straw yield, P uptake, and labile soil residual P concentrations and distribution are reported and discussed in relation to agronomic implications of P placement strategies.

3.2 Abstract

Phosphorus fertilizers are generally placed in the seed row with the seed of annual crops in Saskatchewan at lower rates (i.e. < ~20 kg P_2O_5 ha^{-1} depending on crop tolerance). However, due to desire to increase operational efficiency by reducing fertilizer handled during the seeding operation, and to apply larger amounts of P fertilizer without risking injury, pre-seeding broadcasting and banding is receiving increased interest as a method of P application. A field trial was conducted on a well-managed Brown Chernozem (Echo Association) field near Central Butte, SK on two representative slope positions (upper and lower) within the field. Cropping history of the field was wheat-canola-pea rotation under long-term (20 years) no-till with P fertilizer applied every year at recommended rates. The P treatments evaluated in the trial were seed row placed, deep banded below seed, broadcast and incorporated at 20 kg P_2O_5 ha^{-1}, and broadcast alone at 20, 40, and 80 kg P_2O_5 ha^{-1}. An unfertilized control was included in the comparison. The available P at the site was ranked as moderate to high based on modified Kelowna (KM) extraction. Treatments were applied each year with hard red spring wheat (*T. aestivum* var. Waskada) grown in 2015 and argentine canola (*B. napus* LL252) in 2016. In 2015, crop growth was limited by drought conditions from May to July, with slope position as the only parameter having a significant effect on wheat yield. In 2016 with good growing conditions, canola P uptake was significantly (P=0.0304) higher at the 80 kg P_2O_5 ha^{-1} rate, but there were no significant effects of placement method on yield or P uptake. This is attributed to the inherently good P fertility status of the soil, such that placement of P was not important in affecting crop response. Soil available P content (KM, water extractable, resin exchangeable) in the top 30-cm post-harvest was not significantly different among placement methods but was greatest at the high rate of broadcast P (80 kg P_2O_5 ha^{-1}). From an agronomic management standpoint, where soil P levels are near sufficient, the application of P fertilizer at rates to account for previous crop removal may be the desirable approach, without expectation of a yield response. In soil with inherent good P fertility such as in this study, application method is less important from an agronomic standpoint, and changes to application method could be a viable method of increasing operational efficiency. Further studies should be conducted on a wider variety of soil types, climatic conditions and soil available P levels to confirm these findings.

3.3 Introduction

Application of P (phosphorus) fertilizer is critical to maximize crop growth in soils of low P status. Method of P fertilizer application, commonly termed "placement", can profoundly influence the efficiency of crop utilization and yield response to applied fertilizer P, largely as a result of the immobility of P in the soil (Havlin et al., 2014). Phosphorus fertilizers are generally placed in the seed row with the seed at the time of seeding of annual crops in Saskatchewan at lower rates (Government of Saskatchewan, 2016b). However, due to the desire to increase operational efficiency by reducing fertilizer handled during the seeding operation, and to apply larger amounts of P fertilizer without jeopardizing germination and emergence, pre-seeding broadcasting and banding is receiving increased interest as a method of P application. Applying P fertilizer before seeding through either in-soil or surface application may be agronomically effective and provide flexibility. Most studies conducted to date have compared only two different placement methods and have shown variable responses. For example, in Saskatchewan, Mooleki et al. (2010) found little difference in crop response between banded P application and seed placed P in wheat (*T. aestivum*) and Malhi et al. (2008) reported lower yield in seed placed P treatments compared to side-banded P, while May et al. (2008) found no response to placement. These findings suggest that responses to P fertilizer placement will be dependent on soil type, management history and climatic conditions as these influences the quantity of soil P that is accessible to crop roots. It is hypothesized that placement of P fertilizer will have limited effect on crop response on soils of high P fertility.

Grant et al. (2001) reviewed many studies pertaining to P fertilization and nutrition of small grains, concluding that early season P deficiency had major negative impact on crop yield and pointing to the need for placement of P fertilizer to enable early root access in deficient soils. The consequence of the immobility of P in soil is that even under optimum conditions, roots will not be able to access and take up all the P that is applied as fertilizer in a single season (Havlin et al., 2014). Therefore, it is important in P fertilizer management to also consider the influence of management on residual available P levels in the soil. This will impact P requirements for following crops, as well as potential export of P from the soil in water, covered in chapter 4 of this thesis. The effect of application rate is hypothesized to be more important than placement on influencing the content of labile residual P in a prairie soil.

Methods for assessing the soil's inherent ability to buffer and maintain solution P concentration through extraction of "labile" forms are still limited by removal by extractants of somewhat ill-defined solid phase P pools. Furthermore, organic P (P_o) that buffers supply of inorganic P (P_i) through enzymatic hydrolysis is not accounted for in typical soil P tests, as P_o extracted is not measured through routine colorimetry. However, due to low cost per sample, the routine nature of the analysis, and the many studies that use these extractions, they are still widely used. When operationally defined pools are used, it may be more useful to use more than one approach to help reveal the fate of the applied P. In this study, three different assessments of residual available P are utilized: modified Kelowna (KM), water, and anion exchange membrane extraction.

Therefore, with the objective to provide new information on the effects of fertilizer P placement and application rate strategies on crop response and residual soil status in prairie soils, field trials were conducted during the cropping season of 2015 and 2016 on a typical well-managed, no-till field with good soil P fertility in south-central Saskatchewan. The research trials complement previous work by Weiseth (2015) who examined responses to placement on an adjacent poorly managed field with a history of frequent tillage and erosion, cereal monoculture, and little or no P fertilizer applications made in the past. Three in-soil methods of MAP (monoammonium phosphate) fertilizer (11-52-0) application at 20 kg P_2O_5 ha^{-1} were evaluated (seed row, band below seed, broadcast and incorporate) in addition to three rates of broadcast P (20 kg, 40 and 80 kg P_2O_5 ha^{-1}), and a control with no P added. The study examined the response of hard red spring wheat (*T. aestivum* var. Waskada) in 2015, and canola (*B. napus* var. LL 252) in 2016.

3.4 Materials and methods

3.4.1 Site description

The site used for the field trial was approximately 2-km north of Central Butte, SK, Canada. The soil at the site is loamy in texture, predominantly of the Echo soil association (Ayres et al., 1985) in lower slopes, mixed with Haverhill association in upslope areas. The Echo association soils are solodized solonetz soils with hardpan Bnt horizons while Haverhill association soils are Chernozemic in nature with distinct brown Bm horizons. Due to the saline nature of the parent material, small areas of salinity associated with discharge zones at the toe

slopes were present within the field, but the study area was mostly non-saline (Table 3.1). Trials were conducted separately on two slope positions, upper and lower, within the field to provide a representation of the general topography and soils of the field and its influence on crop response to P placement (Fig. 3.1). Both slope positions had relatively high extractable P and K and moderate contents of extractable nitrate and sulfate in the 0- to 15-cm depth (Table 3.1). All nutrient levels were lower in the 15- to 30-cm depth than in the 0- to 15-cm depth with the exception of sulfate, consistent with presence of sub-soil sulfate salts as indicated by the higher EC (electrical conductivity) values at depth. The soil organic C (carbon) concentrations were typical of the Brown soil-climatic zone (1-2% organic C), with slightly higher organic C concentration in the lower slope position, typical of catenas in Saskatchewan (Pennock and de Jong, 1990; Pennock et al., 2011).

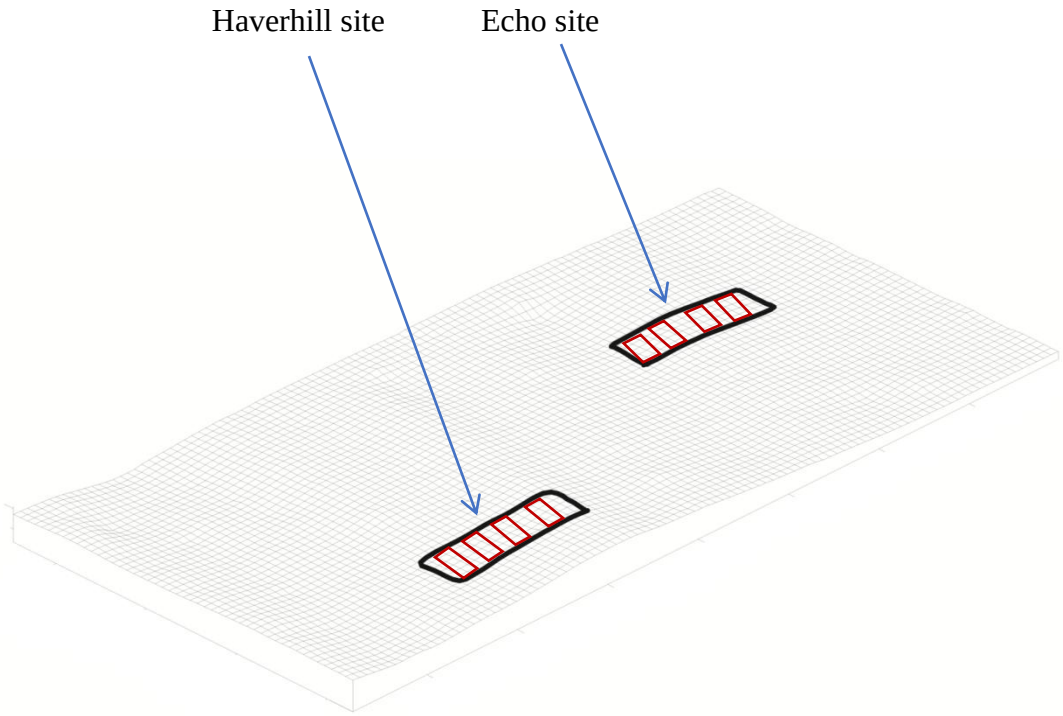


Figure 3.1: Elevation map of P placement study located near Central Butte, SK. Four blocks were placed on the Haverhill site and four on the Echo site. Red boxes depict blocks.

A 0.01 M $CaCl_2$ extraction was done to determine background N and S levels (Houba et al., 2000). Briefly, 20.00 g of soil was weighed into an extraction bottle. 40 mL of 0.01 M $CaCl_2$

was added. The suspension was shaken for 30 min. at 142 rpm. The suspension was filtered through Whatman #42 filter paper and analyzed for NO_3-N and SO_4-S content.

Table 3.1: Extractable nutrients, pH, electrical conductivity (EC) and organic carbon concentration at P placement study sites located near Central Butte, SK. Values are means of 8 core samples collected across each site in May 2015. NO_3-N and SO_4-S extracted by 0.01M $CaCl_2$ (Houba et al., 2000). P and K extracted by Modified Kelowna (Qian et al., 1994). pH and EC measured on 1:2 soil water suspension. Organic C measured using LECO® combustion analyzer

Site	Depth	NO_3-N	P	K	SO_4-S	pH	EC	Organic C
	(cm)	----------kg ha^{-1}----------					dS m^{-1}	%
Haverhill	0-15	9	30	703	12	7.2	0.15	1.35
	15-30	7	7	299	31	8.0	0.41	0.78
Echo	0-15	9	32	684	14	6.5	0.12	1.46
	15-30	7	6	362	52	7.3	0.29	0.87

3.4.1.1 Experimental Design

The experiment was set up as randomized complete block design. The treatments (Table 3.2) were set up as blocks of randomized treatments with four blocks (replicates) at each of the sites. The treatments consisted of a control with no P added, three in-soil treatments (seed row placed (SP), deep banded below seed (DB), and broadcast and incorporated (B/I)) at 20 kg P_2O_5 ha^{-1}, and three broadcast alone treatments (broadcast at 20, 40, and 80 kg P_2O_5 ha^{-1} (B(20), B(40), B(80) respectively)) on 1-m x 3-m plots. The deep band treatment was banded approximately 2.5-cm directly below the seed row at the time of seeding. Seed placed P was placed directly into the seed row at the time of seeding. All broadcast treatments, including the B/I, were done immediately prior seeding. Each site was blocked four times. Treatments were applied on the same plot for two consecutive cropping seasons.

Table 3.2: Summary of P fertilizer treatments used in P placement study. The phosphorus source used was mono ammonium phosphate (MAP) with numeric analysis of 11-52-0.

Treatment	Abbreviation	Placement Category	P_2O_5 Rate
Control	C	-	-
Seed placed	SP	In-soil	20 kg ha^{-1}
Deep banded below seed	DB	In-soil	20 kg ha^{-1}
Broadcast and incorporated	B/I	In-soil	20 kg ha^{-1}
Broadcast at 20	B(20)	Broadcast	20 kg ha^{-1}
Broadcast at 40	B(40)	Broadcast	40 kg ha^{-1}
Broadcast at 80	B(80)	Broadcast	80 kg ha^{-1}

The source of P fertilizer in this study was MAP (11-52-0). Prior to seeding, N fertilizer was applied as urea (46-0-0) broadcast and incorporated across all plots at a blanket rate of 100 kg N ha^{-1}, with specific MAP treatments having urea rates reduced to account for N added in the MAP. In 2016 additional S was applied for the canola crop using potassium sulfate (0-0-47-17) applied to supply 17 kg S ha^{-1} S and 47 kg K_2O ha^{-1}.

3.4.2 Field operations

3.4.2.1. Treatment preparation

Immediately prior to application of the P fertilizer treatments, urea and potassium sulfate were broadcast at the rate described above. On the B/I treatment, MAP was also broadcast prior to roto-tilling to approximately 5-cm depth. Each site was roto-tilled to incorporate the broadcast fertilizer to approximately 5-cm depth. Each plot was then rolled with a hand roller to provide a firm, level seed bed for seeding. For the DB treatment, the application of the MAP band occurred after rolling just prior to seeding, to produce a band that is located ~ 2.5-cm below the seed row. After rolling, the broadcast applications of MAP were made at rates described in table 3.2. Once the broadcasting was complete, the site was seeded. For the seed row placed fertilizer P treatment, the fertilizer MAP was placed in the seed row furrow with the seed at the depth of seeding.

3.4.2.2 Seeding

The sites were seeded with each plot having 3 seed rows of 3-m length with 25-cm row spacing, seeded using a manual double disc seeder. In 2015, the site was seeded on May 6 with HRS Waskada wheat (*T. aestivum*) at a depth of approximately 2.5-cm. In 2016, the site was seeded May 4 with LL 252® canola (*B. napus*) at a depth of approximately 1.25-cm.

3.4.2.3 Weed control

Weed control in 2015 was conducted as a pre-emergence non-selective burnoff with glyphosate followed by an in-crop application of broadleaf and grassy herbicide. On May 7, 2015, glyphosate was applied at a rate of 288 g a.e. ha^{-1}. For in-crop weed control, fluroxypyr was applied at a rate of 80 g a.e. ha^{-1}, 2, 4-D ester at a rate of 158 g a.e. ha^{-1}, and clodinafop at a

rate of 23 g a.i. ha^{-1}. As precipitation was limited, weed populations were low. Due to the saline nature of the site, some kochia proliferated in the Echo site, affecting some plots.

In 2016 precipitation was higher leading to higher weed populations but weed control was effective. A pre-seed burnoff was applied on April 29 using glyphosate at a rate of 178 g a.i. ha^{-1} and carfentrazone at a rate of 3.6 g a.i. ha^{-1}. In-crop herbicide application was made on June 11 using 162 g a.i. ha^{-1} of glufosinate ammonium and 60 g a.i. ha^{-1} clethodim.

3.4.2.4 Climate data

Table 3.3 summarizes climate data for the 2015 and 2016 growing seasons (May to September) in the Central Butte study area, based on meteorological data collected from a station located 15 km south-east of the research site. Temperatures were comparable to historical averages, but with July and August daily high temperatures in both years being lower than historical. Differences were larger in precipitation. In 2015, precipitation in May and June was less than 10% of the historical average, but was more than 3x greater in July, with most of the precipitation occurring in the last week of July. Precipitation was much greater in 2016, with precipitation up to 2x higher than the historical monthly precipitation in the 2016 growing season (Table 3.3).

Table 3.3: Climatic data for Central Butte study area in 2015 and 2016. Values were compared to historical averages from 1981-2010 at the Elbow, SK weather station (Environment Canada).

Month	Average Daily High 2015	Average Daily High 2016	Historical Daily High	Monthly Precipitation 2015	Monthly Precipitation 2016	Historical Monthly Precipitation
	----------°C----------			----------mm----------		
May	19.9	20.6	17.5	2.7	107.6	50.4
June	23.9	23.9	21.8	6.3	70.2	78.9
July	24.3	24.6	25.6	142.5	88.9	53.4
August	24.4	23.1	25.2	32.9	52.5	45.2

3.4.2.5 Harvest

Both the 2015 wheat and 2016 canola crops were hand harvested using a sickle by taking 2-m row lengths from each plot. Crops were cut at similar heights and bagged in cloth bags on-site. In 2015, the wheat was harvested on August 12 and the bags transported to Saskatoon where they were placed in a drying room at ~ 28^{o}C at the University of Saskatchewan. Similarly, 2

metre rows of canola were harvested on August 16, 2016, placed in cloth bags and dried in Saskatoon. Once dried, the samples were ready for processing.

3.4.2.6 Crop processing

Dry samples were first weighed to obtain total above-ground biomass (straw + grain) weights. Once weighed, samples were then threshed and cleaned on a sieve. During threshing, a sub-sample of straw was collected and ground for nutrient analysis. Cleaned samples were weighed to obtain grain yields. Straw yield was then calculated as the difference between total biomass and grain yield. Grain samples were ground using a NutriBullet® grinder and a subsample was taken for grain nutrient analysis conducted using acid digestion described in section 3.4.3.2 below.

3.4.2.7 Soil sampling

After harvest, soil samples were collected in the first week of September each year using a hydraulic punch. Two core samples were taken from each plot (one in the seed row and one in between) and combined for respective depths. In 2015, samples were collected at depth increments of 0- to 15-cm, 15- to 30-cm, and 30- to 60-cm. In 2016, sampling depths were altered to provide a better characterization of soil P in the vicinity of the soil surface, with depth increments of 0- to 5-cm, 5- to 10-cm, and 10- to 30-cm taken. Soil samples were bagged and immediately frozen at -20^{o}C until further processing. Samples were then thawed and allowed to air-dry at 30^{o}C for one week and then ground using a flail grinder to pass through a 2-mm sieve. Dried and ground samples were stored at room temperature until laboratory analysis.

3.4.3 Laboratory analyses

3.4.3.1 Soil analyses

Water extractable P

Water extractable P is useful as a tool to measure biologically available orthophosphate and also provide an index of P potentially transported by water. The water extractable P fraction was determined according to the procedure outlined by Schoenau and Huang (1991). A soil:water ratio of 1:50 was prepared by adding 2 g of soil into a 100 mL plastic container, to which a 100 mL aliquot of distilled water was added. The containers were shaken at 200 rpm for

1 h and then decanted through a Millipore™ filter (pore size 0.45-µm) to obtain a clear extractant. The filtered water samples were then analyzed colorimetrically (Murphy and Riley, 1962).

Anion Exchange Membrane P

The anion exchange membrane extractable P, or "sandwich" P, is a modification of the method described by Qian and Schoenau (2002) to measure exchangeable orthophosphate P in soil. Qian et al. (2008) modified the extraction to achieve an easily replicable nutrient supply rate proxy. In this method, prior to extraction, anion exchange resin membrane strips are placed in a 0.5 M $NaHCO_3$ solution and shaken for 2 h. The procedure was repeated four times, with fresh solution at each interval, for a total of 8 h. The strips were then transferred into DI water until use. For each sample, two 7-dram vial lids were filled with soil to form a small mound above the cap line, ensuring good resin to soil contact. Each cap was then brought to field capacity with DI water using an analytical balance. A charged anion strip was placed on one soil-filled cap and covered by the other one, creating contact on both sides of the resin strip. Parafilm® was then wrapped around the caps to create the sandwich and enable exchange of bicarbonate with soil orthophosphate ions for 24 h. After 24 h, the sandwiches were unwrapped and any soil adhering to the membrane was washed off. The resin strips were then placed into a 7-dram vial and eluted using 20 mL of 0.5 M HCl for 60 min, after which the resin strips were removed and the eluting solution was measured for PO_4 using Murphy and Riley (1962) colorimetry.

Modified Kelowna Extraction

A KM extraction was performed on soil samples after each cropping season of the study according to the method outline by Qian et al. (1994). In this method, 30 mLs of KM solution (0.025 N HOAc, 0.015 N NH_4F, and 0.25 N NH_4OAc) was added to 3 g of air-dried soil. The suspension was shaken at 142 rpm for 5 minutes and filtered through VWR 454 filter paper. The extracting solution was then measured for orthophosphate P content using automated colorimetry on a Technicon Autoanalyzer®.

3.4.3.2 Plant analyses

Ground crop grain and straw samples were analyzed for P and N concentrations using a hot sulfuric acid-peroxide digest (Thomas et al., 1967). In this procedure, ground samples of 0.2490-0.2509 g were weighed and transferred into a digestion tube and 5 mL of concentrated sulfuric acid (18 M) added. The sample was then heated using a heating block to 360° C for 30 min. After heating, the tubes were removed and allowed to cool for 20 min. Once cooled, 0.5 mL of 30% w/w H_2O_2 was added to the tube and vortexed. The solution was then heated on the heating block for another 30 min. These steps were repeated until the colour disappeared from the tubes (approximately 8 times). When the solution was colorless, H_2O_2 was added once more and the solution heated for 60 min. to remove remaining H_2O_2. Once allowed to cool for at least 20 min, each sample was then vortexed and brought to volume (75 mL) using DI water. The tubes were then capped and inverted to homogenize the solution. The final extract was analyzed using automated colorimetry for P and N (NH_4^+) on the Technicon® autoanalyzer. Grain and straw P uptake was calculated by multiplying the P concentration measured in the plant material by the yield.

3.4.4 Statistical analysis

Variables measured included those assessed directly and also calculated from other known variables. The equations used to calculate straw yield, P and N uptake, P recovery, and P yield efficiency are as follows:

$$\text{Straw yield} = \text{total biomass} - \text{grain yield} \quad \text{(Eq. 3.1)}$$

$$\text{Nutrient uptake} = (\text{straw concentration} * \text{straw yield}) + (\text{grain concentration} * \text{grain yield}) \quad \text{(Eq. 3.2)}$$

$$\text{P fertilizer recovery} = \frac{\text{treatment P uptake} - \text{control P uptake}}{\text{P application rate}} \quad \text{(Eq. 3.3)}$$

$$\text{P yield efficiency} = \frac{\text{treatment yield} - \text{control yield}}{\text{P application rate}} \quad \text{(Eq. 3.4)}$$

Statistical analyses were conducted using SAS 9.3 software (SAS Institute Inc, 2012). The study was analyzed as an RCBD with P placement and slope position as the fixed effects

and block as a random effect. A two-way ANOVA was conducted using PROC mixed with means separations using the Tukey-Kramer honest significant difference (HSD) method, where $\alpha=0.05$ for plant parameters and $\alpha=0.10$ for soil parameters due to the hetergeneous nature of P distribution in soil. Outliers were detected using Grubbs test and removed. Specific information on which samples were removed can be found in the appendix (Tables A1-A3). Residuals analysis, to determine if the assumptions of the ANOVA were correct, was conducted using PROC UNIVARIATE in SAS. Residuals were declared not normally distributed if the Shapiro-Wilk *p* value was less than 0.05. Where residuals were not normally distributed, residuals were plotted to determine if data transformations were appropriate. If appropriate, transformations were conducted and analyzed using PROC mixed. Where transformations were not applicable, PROC NPAR1WAY was used to generate Wilcoxon scores to separate means, rendering the interaction effects incalculable. Orthogonal contrasts were performed to compare in-soil treatments to broadcast treatments across a variety of variables. Where applicable, a two-sample t-test was conducted using PROC TTEST. When residual was not normally distributed, Wilcoxon scores were generated using PROC NPAR1WAY to detect differences.

3.5 Results

3.5.1 2015 field season

As shown in Table 3.4, slope was the only significant variable affecting the 2015 wheat crop parameters (Table 3.4). Phosphorus fertilizer treatment and its interaction with slope was not significant for grain and straw yield, N and P uptake, and P recovery efficiency. The slope effect was significant for grain and straw yield, as well as N and P uptake. These effects can be explained by the extremely dry period from May to end of July in 2015, limiting fertility treatment effects and reflecting mainly differences in soil type, with the solonetzic characteristics of the Echo soil restricting root volume and available water. As a result, wheat grain and yield at Central Butte were significantly greater on the Haverhill site but did not differ between treatments (Table 3.4; Fig. 3.2). The same trend was observed for crop P uptake and N uptake (Figs. 3.3, 3.4). Mean yields for the individual P fertilizer treatments in each slope position site can be found in the Appendix (Table A4, Figs. A1, A2).

Table 3.4: Type 3 fixed effects ANOVA summary table of wheat crop parameters measured in the P placement study in 2015. Reported values are *p* values.

Effect	Parameter				
	Grain Yield	Straw Yield†	N Uptake	P Uptake	P Recovery Efficiency
Treatment	0.3987	0.7510	0.7180	0.5511	0.5762
Slope	**0.0010**	**0.0050**	**0.0233**	**0.0398**	0.5830
Treatment*Slope	0.1681	-	0.4204	0.5700	0.9040

†As residuals were not normally distributed, treatment and slope effect were calculated using Wilcoxon scores.

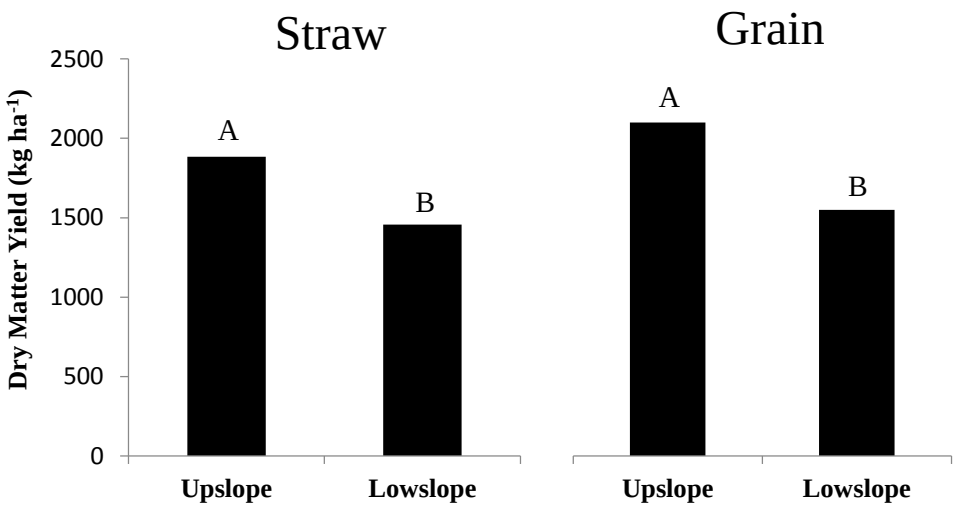


Figure 3.2: Straw and grain (B) yield at P placement trials in 2015. Means were separated using Tukey's protected HSD (α=0.05). For a crop parameter, bars with a different letter are significantly different.

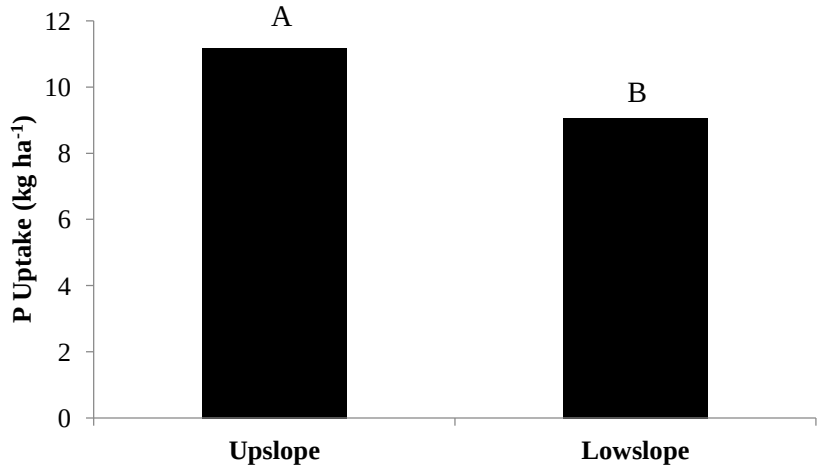


Figure 3.3: Wheat P uptake (grain + straw) in 2015 P placement trials. Means were separated using Tukey's protected HSD. Bars with the same letter are not significantly different at α=0.05.

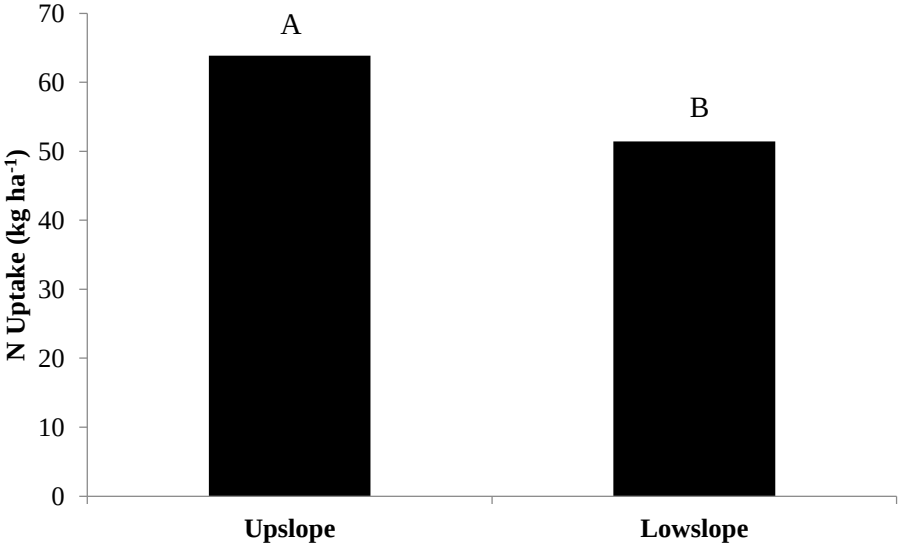


Figure 3.4: Wheat N uptake (grain + straw) in 2015 P placement trials. Means were separated using Tukey's protected HSD. Bars with the same letter are not significantly different at α=0.05.

Residual available soil P in fall after harvest in 2015 was generally not different among treatments, except for membrane extractable P at the 15- to 30-cm depth which was highest in the B(80) treatment. The effect of rate evident deeper in the soil profile may reflect some movement of unused fertilizer P deeper in the profile later in the season, associated with the high amount of rainfall received at the end of July in 2015. The membrane exchangeable P is mainly

orthophosphate in soil solution plus weakly held exchangeable P on soil colloid surfaces (Qian and Schoenau, 2002).

Table 3.5: Modified Kelowna (KM), water soluble, and anion exchange membrane extractable soil P after wheat harvest in 2015. Means followed by the same letters within are row are not different at α=0.10. Unless otherwise specified P rate was 20 kg P_2O_5 ha^{-1}.

Extraction	**Site**	**Depth**	**Treatment**							
		(cm)	C‡	SP	DB	B/I	B(20)	B(40)	B(80)	*p* value
KM P ($kg\ ha^{-1}$)	Haverhill	0-15	15.6 [a]	17.0 [a]	16.8 [a]	15.6 [a]	15.1 [a]	18.0 [a]	20.1 [a]	0.8883
		15-30	5.2 [a]	4.4 [a]	4.6 [a]	4.9 [a]	4.7 [a]	4.1 [a]	4.4 [a]	0.7598
	Echo	0-15	9.7 [a]	12.7 [a]	7.9 [a]	9.1 [a]	6.7 [a]	6.5 [a]	9.8 [a]	0.2645†
		15-30	4.4 [a]	4.6 [a]	4.6 [a]	5.6 [a]	4.1 [a]	4.6 [a]	4.2 [a]	0.4073
Water Soluble P ($kg\ ha^{-1}$)	Haverhill	0-15	5.6 [a]	5.8 [a]	5.8 [a]	5.1 [a]	4.6 [a]	6.8 [a]	7.8 [a]	0.4667†
		15-30	1.0 [a]	0.5 [a]	0.6 [a]	0.9 [a]	0.9 [a]	0.7 [a]	0.8 [a]	0.4569
	Echo	0-15	25.3 [a]	45.7 [a]	26.4 [a]	22.6 [a]	17.3 [a]	20.0 [a]	25.3 [a]	0.1740
		15-30	0.6 [a]	1.4 [a]	1.0 [a]	1.0 [a]	0.8 [a]	1.3 [a]	1.8 [a]	0.8771†
Membrane Exchangeable P ($\mu g\ cm^{-2}\ day^{-1}$)	Haverhill	0-15	0.63 [a]	0.50 [a]	0.58 [a]	0.34 [a]	0.44 [a]	0.57 [a]	0.84 [a]	0.5071
		15-30	**0.07 [ab]**	**0.03 [b]**	**0.03 [b]**	**0.05 [ab]**	**0.02 [ab]**	**0.04 [b]**	**0.11 [a]**	**0.0321**
	Echo	0-15	0.40 [a]	0.96 [a]	0.78 [a]	0.83 [a]	0.61 [a]	0.42 [a]	0.69 [a]	0.2645
		15-30	0.03 [a]	0.04 [a]	0.03 [a]	0.04 [a]	0.03 [a]	0.07 [a]	0.04 [a]	0.4291

†As residuals was not normally distributed, treatment and slope effect were calculated using Wilcoxon scores.

‡C=control (no P), SP=seed placed, DB=deep banded, B/I=broadcast and incorporated, B(20, 40, 80)=broadcast at 20, 40, and 80 kg P_2O_5 ha^{-1} respectively.

3.5.2 2016 field season

For the 2016 canola crop, across most measured parameters there was no significant effect of treatment or slope position site (Table 3.6). Canola grain yields ranged from ~3500 to 5100 kg ha^{-1}. Canola grain yields for all treatments at the two slope position sites are shown in Appendix (Fig. A2). The only crop parameter significantly influenced by treatment was P uptake (Table 3.6, Fig. 3.5). P uptake was higher in fertilized treatments and appeared to be more influenced by rate than by placement, as the only significant (p<0.05) difference is between the C and B(80) treatments. The higher P rate over two subsequent years along with higher rainfall in 2016 explains the increased canola P uptake, but without increasing yield (luxury uptake).

Table 3.6: Type 3 fixed effects ANOVA summary table of canola crop parameters measured in the P placement study in 2016. Reported values are *p* values.

	Parameter				
Effect	Grain Yield	Straw Yield†	N Uptake	P Uptake	P Recovery Efficiency
Treatment	0.7582	0.5318	0.8649	**0.0304**	0.9844
Slope	0.6159	0.4363	0.6598	0.6303	0.9389
Treatment*Slope	0.6660	-	0.7949	0.5879	0.8859

†As residuals were not normally distributed, treatment and slope effect were calculated using Wilcoxon scores.

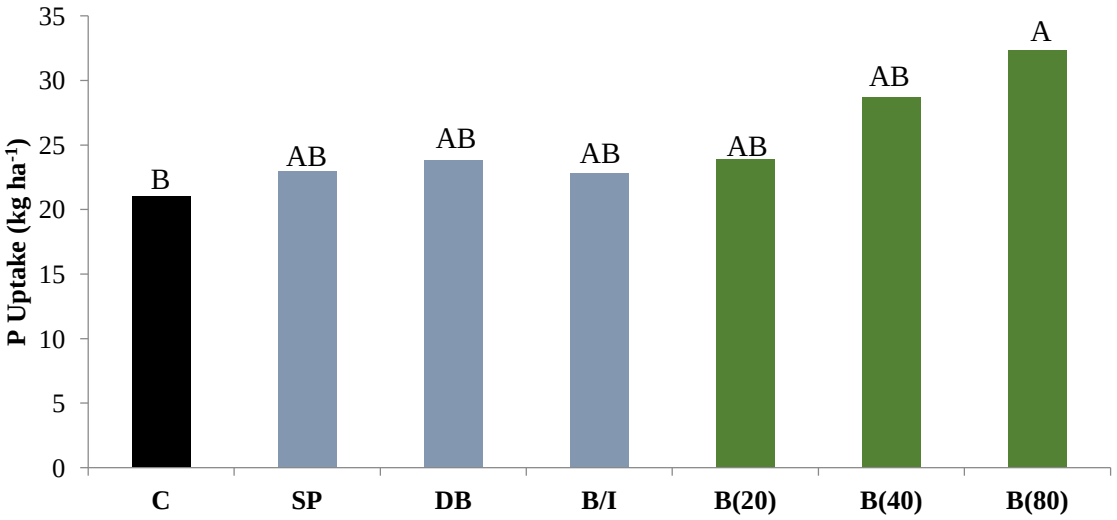


Figure 3.5: Canola P uptake in 2015 P placement trials. Means were separated using Tukey's protected HSD. C, SP, DB, B/I, B denote control (no P), seed-placed, deep banded, broadcast and incorporate and broadcast respectively. Rate of P added (kg P_2O_5 ha^{-1}) in parentheses**.** Unless otherwise specified, the P rate was 20 kg P_2O_5 ha^{-1}. Bars with the same letter are not significantly different at α=0.05.

The 2016 post-harvest soil extractable P levels (Table 3.7) showed more differences than in 2015, as expected from two successive years of treatment application. For all extractants, more differences in residual soil labile P were evident in the 5- to 10-cm depth increment, which is approximately where any residual bands of fertilizer and root depletion zones would be in the soil. The B(80) treatment had generally highest residual P of the fertilizer treatments. This is to be expected based on rate alone.

Table 3.7: Extractable P from P Placement trial in 2016. Separation of means where p value is significant was performed using Tukey's HSD. Means followed by the same letters within are row are not different at α=0.10. KM=modified Kelowna. Unless otherwise specified P rate was 20 kg P_2O_5 ha^{-1}.

Extraction	**Slope**	**Depth**	**Treatment**[†]							
		(cm)	C	SP	DB	B/I	B(20)	B(40)	B(80)	*p* value
KM P (kg ha^{-1})	Haverhill	0-5	12.8 [a]	16.1 [a]	16.8 [a]	19.0 [a]	17.2 [a]	15.3 [a]	20.7 [a]	0.5015
		5-10	7.6 [a]	7.7 [a]	8.7 [a]	10.0 [a]	10.4 [a]	9.9 [a]	14.0 [a]	0.1623
		10-30	**13.5** [ab]	**12.0** [ab]	**10.5** [b]	**10.7** [b]	**15.4** [ab]	**12.2** [ab]	**16.8** [a]	**0.0398**
	Echo	0-5	**15.4** [b]	**23.4** [ab]	**17.7** [b]	**17.0** [b]	**19.8** [b]	**29.0** [ab]	**36.1** [a]	**0.0031**
		5-10	**8.7** [b]	**11.2** [ab]	**10.0** [ab]	**8.9** [b]	**7.2** [b]	**14.2** [ab]	**19.4** [a]	**0.0226**
		10-30	9.7 [a]	10.7 [a]	11.8 [a]	14.4 [a]	11.2 [a]	11.7 [a]	10.2 [a]	0.5110
Water Soluble P (kg ha^{-1})	Haverhill	0-5	3.8 [a]	4.6 [a]	2.5 [a]	5.7 [a]	4.1 [a]	4.8 [a]	7.3 [a]	0.1332
		5-10	**0.9** [b]	**1.5** [ab]	**2.3** [ab]	**2.6** [ab]	**1.8** [ab]	**2.7** [ab]	**3.7** [a]	**0.0875**
		10-30	**0.6** [b]	**0.4** [ab]	**0.3** [b]	**0.2** [b]	**2.8** [a]	**1.4** [ab]	**1.9** [ab]	**0.0181**[‡]
	Echo	0-5	4.5 [a]	4.9 [a]	4.5 [a]	4.2 [a]	5.9 [a]	7.3 [a]	7.9 [a]	0.2380[§]
		5-10	2.5 [a]	4.6 [a]	3.1 [a]	2.6 [a]	2.0 [a]	5.7 [a]	4.8 [a]	0.1958
		10-30	2.6 [a]	2.5 [a]	3.1 [a]	2.1 [a]	2.9 [a]	7.5 [a]	2.6 [a]	0.2221[§]

Table 3.7 cont.

Extraction	Slope	Depth	C[§]	SP	DB	B/I	B(20)	B(40)	B(80)	*p* Value
Membrane Exchangeable P (μg cm^{-2} day^{-1})	Haverhill	0-5	0.57 [a]	1.12 [a]	0.92 [a]	0.85 [a]	1.08 [a]	0.79 [a]	0.63 [a]	0.6948
		5-10	**0.54 [ab]**	**0.46 [b]**	**0.45 [ab]**	**0.70 [ab]**	**0.59 [ab]**	**0.37 [b]**	**1.26 [a]**	**0.0550**
		10-30	0.09 [a]	0.09 [a]	0.05 [a]	0.06 [a]	0.13 [a]	0.12 [a]	0.13 [a]	0.4483
	Echo	0-5	0.39 [a]	0.46 [a]	0.66 [a]	0.37 [a]	1.18 [a]	1.03 [a]	1.22 [a]	0.1070
		5-10	**0.41 [b]**	**0.75 [b]**	**0.60 [b]**	**0.37 [b]**	**0.43 [b]**	**0.75 [ab]**	**1.68 [a]**	**0.0018**‡
		10-30	0.01 [a]	0.00 [a]	0.00 [a]	0.04 [a]	0.02 [a]	0.01 [a]	0.02 [a]	0.2899‡

†C=control (no P), SP=seed placed, DB=deep banded, B/I=broadcast and incorporated, B(20, 40, 80)=broadcast at 20, 40, and 80 kg P_2O_5 ha^{-1} respectively.
‡As residuals were not normally distributed, a square root transformation was applied
§As residuals were not normally distributed, treatment and slope effect were calculated using Wilcoxon scores.

A comparison in which fertilizer P placements were grouped into in-soil and broadcast (20 kg P_2O_5 ha^{-1}) was conducted for the 2015 and 2016 wheat and canola parameters, similar to the approach used by Weiseth (2015) for his trial with soybeans on a P deficient soil. The results of the analysis are shown in Table 3.8

Table 3.8: *P* values from a comparison of in-soil P fertilizer treatments vs broadcast treatment using a two sample t-test. Differences were declared significant at α=0.05. Calculations for uptake, P recovery, and P yield efficiency can be found in section 3.2.5.

Year	Slope	Straw Yield	Grain Yield	N Uptake	P Uptake	P Recovery	P Yield Efficiency
2015	Haverhill	0.4262	0.3519	0.3180	0.7630	0.5046	0.4715
	Echo	0.2249†	0.8176	0.5000†	0.7040	0.3691†	0.4784
2016	Haverhill	0.1325	0.4883	0.2379	0.0729†	0.5385	0.8113
	Echo	0.2249†	0.4885†	0.7701	0.9778	0.9403	0.2943†

†As residuals were not normally distributed, Wilcoxon scores were used to determine *p* value.

No significant differences were observed between in-soil and broadcast treatments at 20 kg P_2O_5 ha^{-1} rate in both 2015 and 2016 (Table 3.9). This is in contrast to findings of Weiseth (2015) who grew soybeans on an adjacent P deficient field and found significantly better yield, P uptake and recovery by soybeans with in-soil placement.

3.6 Discussion

3.6.1 Site influences

History of P fertilization at recommended rates, continuous cropping, and utilization of no-till to eliminate erosion for several years prior to the experiment in the study field is likely a main contributor to the general lack of crop response to P fertilizer placement. Drought conditions were also likely a contributing factor limiting P response in 2015, with lower water availability in the solonetzic Echo soil being the predominant factor affecting yield. The initial high soil test P levels as well as the 2015 drought are important factors explaining the lack of response in the current study compared to Weiseth (2015) working on an adjacent field under

normal moisture conditions but with low P fertility associated with long-term history of little or no P fertilizer applied, extensive tillage induced erosion, and wheat-fallow cropping system. Clearly, management history has an important role in governing overall P fertility and the crop response to P fertilizer placement and rate. If the goal is to simply replace what is removed by the crop on a soil that has high P fertility status to begin with, then for agronomic considerations the P fertilizer placement strategy appears relatively unimportant.

Additionally, as this study was only conducted in one field, the inference space is limited. Ability to compare these results directly to that of Weiseth (2015) are limited because that study examined P response in soybeans. Certainly, comparison to other P fertilization studies with the same crops reported in the literature as used in the current study is useful and is provided in the following section.

3.6.2 Crop response to P placement

The results of this study for wheat response to P placement are corroborated by results reported by others in the literature. For example, Rehm et al. (2003) found that fertilizer P rate was more important than placement for wheat in Minnesota, and Mooleki et al. (2010) also found limited differences among P placement strategies (seed-placed versus band) with wheat in Saskatchewan, similar to this study. Selles et al. (2003) noted the most important effect of P was improving vigor and plant density rather than yield increase and that P placement does not always influence final yield. However, Mooleki (2010) points out placement of P is likely more important in low P soils, as found by Weiseth (2015). In the field used in the 2015 and 2016 study, the available P status according to soil test was double that of the site used by Weiseth (2015) and appeared to be sufficient and non-limiting, resulting in no differences attributable to placement, with rate being an overriding factor promoting what is likely luxury uptake of P by the canola crop grown in 2016 (i.e. increased uptake without increased yield). Grower resource literature, such as that provided by IPNI (1999), assert that crop response to P is different based on placement and that response is different based on crop and climatic conditions. However, this appears to be most evident when low P status and environmental conditions inhibit root access to P. The spring conditions of the current study were generally warm, and cool temperatures limiting diffusion rates and crop uptake were likely not a major factor.

Canola was also unresponsive to P placement in this study. Unfortunately, there are fewer studies of P placement in canola in the literature to compare to. Thomas and Rengel (2002) recommended application of DAP (diammonium phosphate) in a band for canola to limit sorption and tie-up in high P fixing soils. An interesting meta-analysis by Bell et al. (2013) showed deeper placement resulted in higher yields for both canola and wheat in Australia, but environmental and soil conditions are very different there compared to western Canada. While a significant difference was not observed in the current study, there was a trend for extractable P and yield in the deep band treatment to be generally higher than seed placed or broadcast and incorporated treatments. This was also observed by Weiseth for soybean and consistent with the findings of Bell et al. (2013). However, in northeastern Saskatchewan, Nuttal and Button (1990) found no difference between deep banding and seed placement for canola unless the P rate was low. Lemke et al. (2009), comparing seed placement and side banding, reported no response to P placement method on yield of canola in relatively high P testing soils while Karamanos et al. (2002) found seed placment to yield the best on deficient sites. The results from the current study are consistent with the literature, given the relatively high P levels at the site used in this study. Furthermore, the lack of response to placement reinforces the concept that hybrid canola is an effective nutrient scavenger due to prolific root growth. Once established and void of predation and competition threats, canola is stated to have no problem recovering P from the soil if it is present (Canola Council of Canada, 2013).

The response of other crops to P placement often shows limited differences, and where differences do occur they are caused by physiological toxicity. For example, Malhi et al. (2008) found a reduction in flax yield from seed placed P treatments due to the low tolerance and injury to flax from seed row placed P. This is similar to what would be expected in canola, but canola can tolerate a higher seed placed P amount than flax (Saskatchewan Ministry of Agriculture, Guidelines for Safe Rates of Seed Placed Fertilizer). Hemp showed variable response to seed placed P, depending on the crop parameter examined (Vera et al., 2004). The research conducted on P placement methods across all crops has usually been done on low P sites where low solution concentration, buffering ability and diffusion rates limit crop uptake. Where P is sufficiently high, placement of P in the soil does not appear to matter as much.

A review by Grant et al. (2001) concisely highlighted the importance of P supply early in a plant's lifecycle. It was also conveyed that, despite a lack of early season P, the plant was

capable of recovering from deficiency. Early season deficiency can reduce maximum yield potential (Barry and Miller, 1989), but early studies of P supply, particularly in wheat, were based on solution culture studies with inherent limitations (Grant et al., 2001). It is very likely given the high background P levels, that P was not limiting yield production in either year of the study. Furthermore, significant differences that arose from treatments (i.e. P uptake) were based on additional P added and luxury uptake at rates of 80 kg P_2O_5 ha^{-1} added over two years or application.

The limited response to P placement in this field at two topographic positions over two years as well as other studies reported in the literature, highlights that P placement does not have a major influence on crop yield in moderate to high P fertility soils. The agronomic effectiveness of P application method will therefore depend on soil P status, with placement strategy less important as available P status increases. However, other factors such as operational efficiency and environmental considerations (covered in the next chapter) also play into the decision as to the overall best application strategy for P.

3.6.3 Soil residual available P

Crop P fertility prediction and planning is complex, as changes in fertility status are expected to arise over time from either over- or under-applying P fertilizer amounts relative to crop needs and removal as they vary from season to season. This points towards the need to consider residual P and its availability in the soil as part of long-term P fertility management (McKenzie et al., 1992). It is important to recognize that P in the soil can exist in both labile and stable pools in the soil and different extractants may be more or less effective in measuring the fractions (Schoenau et al., 1989). After one year of application, there were no discernable differences in available labile P status in the different treatments in the fall of 2015, showing that at normal application rates, it takes more than one year to significantly alter available P levels in a field. After two years of application, higher application rates of MAP generally resulted in a trend of increased soil P.

The effects of the P fertilizer treatments on residual P were most evident below the top 5-cm of the soil profile. This is explained by placement of fertilizer below these depths as well as some downward movement of surface P with water, especially at high rates, which is covered in more detail in the next chapter. Applying the same rate of 20 kg P_2O_5 ha^{-1} but with different

placement generally had little effect on soil residual available P. Therefore, rate of application appears to be a more important controlling factor than placement method in influencing residual P amounts in the surface of these and similar soils.

3.6.4 Management implications

Broadcasting of P, despite the potential stranding of P on the soil surface, did not affect crop performance compared to in-soil placement in this study. However, the study site was generally unresponsive to P fertilization in general due to management history contributing to high inherent soil P availability. Broadcasting may be appropriate to maintain soil P status and could contribute to operational efficiency, but if P levels are already high environmental effects may also be of concern, and will be covered in detail in Chapter 4. From an agronomic standpoint, based on these results, there appears to be no drawback to applying P fertilizers in different ways if soils are not P deficient and conditions are such that early season supplies of available P to seedling roots are not compromised by conditions like cold temperatures. Therefore, if costs can be recovered over the long term from application for maintenance of P levels, application techniques can be flexible according to producer situation and equipment. P application can be made in amounts that match previous crop removal and thereby maintain high P fertility, being able to draw on these P reserves down the road.

4. SUSCEPTIBILITY OF PHOSPHORUS TO EXPORT WITH WATER AS INFLUENCED BY APPLICATION STRATEGY

4.1 Preface

In Chapter 3 the agronomic effects and producer benefit aspects of various P fertilizer placement strategies were considered. This chapter focuses on the environmental implications of P fertilizer placement, emphasizing potential transport of P off-site in runoff and leaching water as related to P fertilizer placement and rate.

4.2 Abstract

Phosphorus (P) export in agricultural runoff can be an important contributor to eutrophication of adjacent water bodies. Manure application has received more attention than commercial inorganic P fertilizers in the link between P application strategy and the quantity and nature of P lost in water export. This chapter addresses this gap by examining the effect of monoammonium phosphate fertilizer application method, including seed row placed, banded, broadcast and incorporate and broadcast alone (low and high rate), on residual soil P and the amount and composition of P in simulated snowmelt runoff and leachate waters. Soils were collected after harvest from a P placement trial on a well-managed P fertilized Brown Chernozem near Central Butte, SK. Characterization of residual soil P was done by determining available P distribution across the seed bed using intact soil monoliths, along with sequential extraction to examine the influence of P placement and rate on soil P forms. The export of P was examined through simulation of snowmelt runoff and rainfall applied to intact soil slabs and cores, respectively collected from the field. Amounts and forms (inorganic and organic) of P in the water were assessed using chemical methods and ^{31}P nuclear magnetic resonance (NMR) spectroscopy. The distribution of P in the soil after harvest was not significantly affected by P application method. Rate of application appeared to have greater influence on the amount of P exported in snowmelt runoff than the placement method. The largest amounts of total P exported in snowmelt runoff were in the high application rate (80 kg P_2O_5 ha^{-1}) surface broadcast treatments (0.50 kg total P ha^{-1}), with half or less of this amount in the unfertilized and 20 kg P_2O_5 ha^{-1} treatments. The high rate broadcast treatment also had the highest proportion of total P as DRP (dissolved reactive P). The NMR spectroscopic analysis also revealed the dominance of inorganic orthophosphate in the runoff water. The higher rate surface broadcast treatment also had the greatest amount of dissolved inorganic P removed by vertical leaching. The amounts of dissolved inorganic phosphorus (kg P ha^{-1}) calculated to have moved laterally in simulated snowmelt runoff were an order of magnitude or greater than the amount of P moved vertically below 10 cm by leaching water in intact soil cores. The dissolved P concentrations in runoff and leachate waters were above the eutrophication standard for freshwater lakes of 0.01 mg P L^{-1} for all treatments. Fertilizer P applications that are made by broadcasting without incorporation at rates above that which would normally be utilized by the crop in the year of application, such as

the 80 kg P_2O_5 ha^{-1} broadcast treatment, appeared to increase potential export of P in dissolved reactive forms off-site with water in this soil.

4.3 Introduction

Phosphorus runoff, both from mineral fertilizer and organic amendments, can contribute to the eutrophication of surface water bodies. Examples of eutrophied freshwaters include Lake Winnipeg (Lake Winnipeg Stewardship Board, 2006), Lake Erie (Michalak et al., 2013; Scavia et al., 2014), and the Gippsland Lakes (EPA, 1995) in the US. As reviewed in Chapter 2, eutrophication has negative effects on water quality. Measures for reducing P loads from watersheds have been introduced to minimize non-point agricultural runoff contributions. These measures include temporal restrictions on manure application, as well as recommendations for fertilizer P placement in the soil, with broadcasting being the least preferred method (Weiseth, 2015). Manure application has been shown to increase the potential P export in snowmelt runoff from prairie soils, especially cattle manure applied at rates which exceed crop uptake and removal over time (King et al., 2017). Manure management strategies have been evaluated for their influence on P in water for many years (e.g. Sharpley et al., 1994). In recent work by King et al. (2017), placement method (broadcast, broadcast and incorporate, sub-surface band) was shown to have a lesser effect on P and N export in surface runoff than manure type, while in-soil placement in bands was found to increase the P removed in leachate, compared to surface application. However, few studies have evaluated the effects of commercial inorganic P fertilizer application strategy on water P export in prairie soils. The research in this chapter aims to address that gap.

As discussed in Chapter 3, broadcasting is an operationally convenient application technique for maintaining P status without loss of yield in soils of high P fertility. However, in soils of low P fertility, broadcasting typically results in lower P recovery and yield response in the year of application, due to inability of crop roots to access the surface placed P, and the unused P at the surface can contribute to elevated export of P in runoff compared to P fertilizer placed in the soil (Weiseth, 2015). Sustainability issues, important in modern agriculture, are encouraging a holistic approach with considerations for yield, economic return, and environmental impact receiving equal attention. Holistic approaches require comprehensive understanding of all factors affecting agronomics and environmental footprints of the practices. For P and its environmental impacts, this includes both the amounts and the forms in which P is moving. The types of P compounds behave differently in terms of binding strength, solubility, and plant and microbial bioavailability, all important aspects in determining potential

environmental risk. Inorganic P (P_i) minerals found in soil or formed when fertilizer or manures are added will largely reflect the inorganic chemistry of the soil (e.g. Kar et al., 2012), but organic P (P_o) compounds and transformations are generally more difficult to characterize and study.

The objective of the work described in this chapter was to determine how the strategy for application (placement, rate) of MAP (monoammonium phosphate) fertilizer influences:

1) the distribution of P spatially in the soil and chemically among sequentially extracted fractions,
2) the amounts and forms of P exported in simulated snowmelt, and simulated leaching events using intact surface soil slabs and cores collected after harvest in the fall of 2016 from the Central Butte P application study site,
3) to determine if a soil extraction used in chapter 3 was suitable for predicting exported P.

4.4 Materials and methods

4.4.1 Site description

The field used for the study was located 2 km north of Central Butte, SK in the Brown soil zone, with soil in study field mapped as Haverhill/Echo Association. Characteristics of the site, the field experimental design, treatments, plot layout and agronomic, climatic information are all provided in detail in Chapter 3 (section 3.4) and will not be repeated here. Descriptions of treatments can be found in Table 3.2. Simulated snowmelt runoff analysis was conducted on the Haverhill site while the simulated leaching using intact cores was conducted using soils collected from the Echo site.

4.4.2. Spatial distribution of soil P

The technique used to examine spatial distribution of residual P in the surface soil in the fall of 2016 after two years of fertilizer application and cropping followed the protocol of Kar et al. (2012). In this procedure, nailboards with 7.6-cm nails on a 5- x 5-cm grid were used to remove monoliths of 20-cm x 30-cm. A trench around the monolith was excavated and the nailboard was placed into a smooth soil wall. The nailboard was removed from the ground with a

spade as shown in Fig. 4.1. The soils used were the 20 kg P_2O_5 ha^{-1} placement treatments in the Haverhill site.

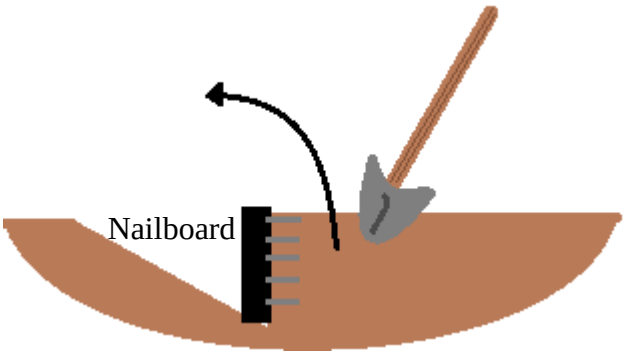


Figure 4.1: Extraction of intact soil monolith using a nailboard and a spade.

Once extracted, each monolith was carefully wrapped and brought to Saskatoon for sub-sampling. Sub-sampling of the monolith was performed with a hand-punch coring device (Fig. 4.2). A grid was established on the monoliths centered on last season's seed row. Samples were taken at the identified seed row location as well as 5-cm and 10-cm horizontally away on either side, and at 1-, 4-, 7-, and 10-cm depths to create a 20-point grid. Subsamples were air dried and analyzed for extractable available P (mg P kg^{-1}) using a modified Kelowna extraction (Qian et al., 1994).

Figure 4.2: Sub-sampling across intact monolith. Samples were taken at grid intersections.

4.4.3 Sequential extraction

The sequential extraction was conducted on surface (0- to 5-cm) soil samples collected from the Haverhill site treatment plots in fall of 2016 as described in section 3.4.3.7. The method used for sequential extraction is described by Tiessen and Moir (2008), with a summary of the process shown in Fig. 4.3. After addition of extractant at each step, soil was re-suspended through shaking.

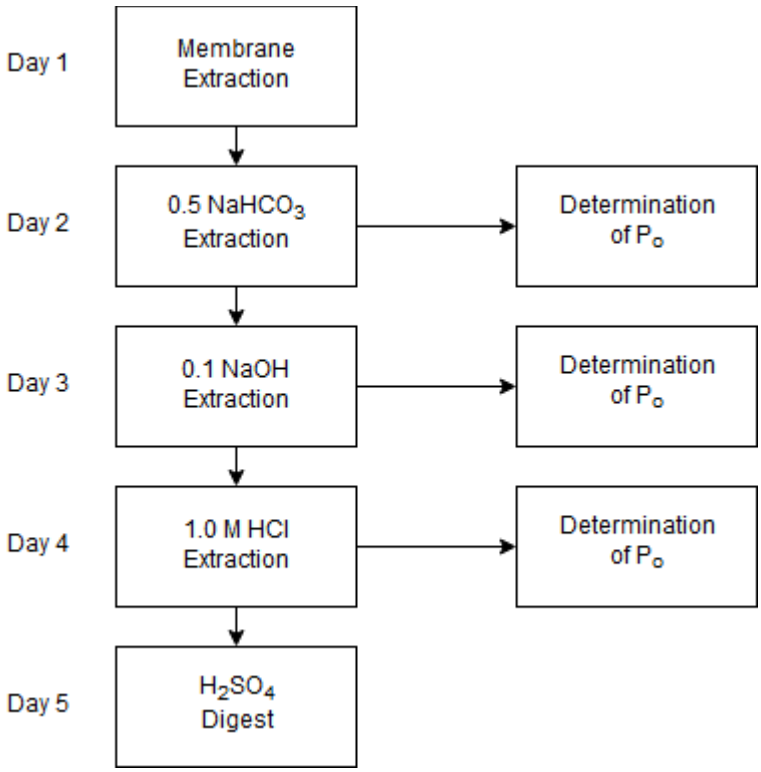


Figure 4.3: Sequential P extraction procedure. P_i is determined directly in each fraction colorimetrically using ammonium molybdate blue method (Murphy and Riley 1962). Total P is determined by digest, with P_o determined by subtracting P_i from P_t.

On the first day, 0.5 g of soil from the 0- to 5-cm depth was weighed into a 50 mL extraction bottle. Then 30 mL of DI water was added along with 2 charged anion exchange membranes (described in Chapter 3). The mixture was then shaken at 100 rpm for 16 h, after which the membranes were removed and transferred into a 16-dram vial for elution using 0.5 M HCl. Details regarding elution can be found in Chapter 3. The suspension was centrifuged at 5 000 *g* for 10 min and the solution was decanted, with the remaining soil to be used for the 0.5 M $NaHCO_3$ extraction.

On day 2, 30 mL of 0.5 M $NaHCO_3$ was added to the extraction bottles and shaken overnight for 16 h. The suspension was then centrifuged and decanted, and the solution vacuum filtered through 0.45-µm membrane filters into 16-dram vials. The solution was then analyzed for P_o and P_i. Soil remaining on the filter paper was returned to the extraction bottle.

On day 3, 1.0 M NaOH was added to the extraction bottles and shaken for 16 h. The next day the suspension was centrifuged and the solution removed using a vacuum filtration system as described above. The remaining soil on the filter paper was returned to the extraction bottle. The extract was then analyzed for P_o and P_i.

On day 4, 1.0 M HCl was used as an extractant and shaken between days 3 and 4 for 16 h. As in days 2 and 3, the samples were centrifuged and vacuum filtered. The solution was analyzed for P_o and P_i.

The remaining soil was transferred to 75 mL digestion tubes and digested using a sulfuric acid digestion. Briefly, 5 mL of H_2SO_4 was added to each tube, along with 0.5 mL H_2O_2. The tubes were heated on a digestion block to 360° C for 30 min, then removed and allowed to cool. This cycle was repeated 8-10 times until the solution was clear, then put on the digestion block for an hour to remove any remaining peroxide. The solution was then brought to volume using DI water and analyzed on the Technicon® autoanalyzer.

Organic P analysis was done using an ammonium persulfate digestion to determine total P. Organic P was operationally defined as the difference between P_t (total P) and P_i. Briefly for the digestion, ammonium persulfate was added to Nalgene® digestion tubes along with extracting solution. Specific amounts varied with the matrix. The solution was autoclaved for one hour using a liquid cycle. The resulting solution was analyzed to determine P_t using colorimetry (Murphy and Riley, 1962).

4.4.4 P export in water assessments

4.4.4.1 Simulated snowmelt runoff

Snowmelt Collection and P Analysis

The simulated snowmelt procedure followed the protocol of King et al. (2017) and is described in detail by King (2015). Intact slabs of soil were collected from a single block of replicates in the upper slope experimental site at Central Butte in October of 2016 by carefully excavating a trench surrounding the slab. The slab was "cut" from below by sliding acrylic glass

(poly(methyl methacrylate)) underneath and removed from the pit. The intact slabs were carefully packaged for transport using plastic wrap, and brought to Saskatoon where they were frozen until analysis (Fig. 4.4). Slabs were extracted to provide a slab of approximately 25-cm length x 20-cm width x 10- to 12-cm deep. Exact dimensions for each slab were recorded and used prior to addition of snow for calculation of surface area.

Figure 4.4: Intact surface soil slab collected from Haverhill P placement site at Central Butte, SK.

Frozen slabs were placed in insulated boxes lined with plastic that funneled the runoff water into plastic buckets (Fig. 4.5). In consideration of NMR (nuclear magnetic resonance) analysis, enough snow was added to provide a desired volume of runoff. Four separate applications of 1 kg of snow enabled the collection of approximately 2.5 L of runoff water for each treatment. Each 1 kg (~7.5-cm) of snow added to the soil slab resulted in the equivalent of about 2-cm of snowmelt water equivalent. The melt was conducted at 19.7° C with 1 kg of snow added every 24 h, with collected runoff frozen between collection periods to avoid microbial transformation of the P in the collected water. Snow for the study was collected immediately after a snowfall event close to Wilcox, SK at N 50° 08.047’ W 104° 36.554’. The snowmelt was analyzed for background P concentrations and this was subtracted from the P measured in the runoff water from the slabs.

Figure 4.5: Intact slab in the insulated box for the simulated snowmelt.

Filtration and fractionation

Prior to analysis, each runoff sample collected was thawed and the volume of runoff measured prior to filtration. The P was operationally defined to be dissolved if it was able to pass through a 0.45-µm filter. Samples were filtered using washed ashed glass 0.45-µm filter paper. Each filter was weighed prior to use and collected and dried after use to determine the weight of particulate matter. A sub-sample was taken of the dissolved fraction for P analysis while the rest was frozen in ice cube trays for freeze drying.

For partitioning of P_o and P_i in the dissolved fraction, an ammonium persulfate digestion (Tiessen and Moir, 2008) was performed on a collected sub-sample of runoff water for each treatment as described above. Briefly, 0.4 g of ammonium persulfate was added to an aliquot of runoff. The mixture was autoclaved for an hour, after which it was analyzed colorimetrically to determine P_t. For P_i measurement (DRP), colorimetry was done directly on the water samples. Organic P DURP (dissolved unreactive phosphorus) was calculated as:

$$\text{Dissolved Organic P} = \text{Total Dissolved P} - \text{Dissolved Inorganic P} \qquad \text{(Eq. 4.1)}$$

For determination of particulate P, particulates on the glass filter paper were extracted using 0.25 M NaOH and 0.05 M Na_2EDTA and shaken for 4 hours. Samples were centrifuged for 10 minutes at 10 000 *g* and the solution decanted into test tubes. A 1-mL aliquot was removed, diluted to 10 mL with deionized water, and analyzed using inductively coupled plasma atomic emission spectroscopy for P, Al, Fe, Ca, and Mn. The remaining sample was frozen in the

tube on its side to be freeze dried, as increased surface area increased the rate of sublimation. From the sample volume and concentration, as well as slab volume, amount of P runoff could be calculated as:

$$\text{Area adjusted runoff P} = \frac{\text{P concentration} * \text{runoff volume}}{\text{slab area}} \qquad \text{(Eq. 4.2)}$$

Flow weighted means of P runoff were calculated as follows:

$$\text{Flow weighted mean} = \frac{\text{total P in runoff}}{\text{volume of runoff}} \qquad \text{(Eq. 4.3)}$$

Solution ^{31}P NMR spectroscopy

Runoff water samples were first freeze-dried to concentrate the sample. Once freeze dried, the samples were analyzed by solution P-NMR spectroscopy using a modified version of Cade-Menun and Preston (1996). In preparation for analysis on the NMR, the freeze-dried sample was resuspended in 0.65 mL D_2O, 0.4 mL of 10 M NaOH, 0.65 mL of the NaOH-EDTA extracting solution, and 0.65 mL of deionized water, centrifuged (20 min, 1500 *g*) and transferred to 10-mm NMR tubes. Solution P-NMR spectra were acquired on a Bruker Avance 500 MHz NMR spectrometer with a 10-mm broadband probe. The NMR experimental parameters were: 45° pulse angle, 0.5 s acquisition time, 7.5 s pulse delay for particulate samples, 11.5 s pulse delay for filtrate samples, no spinning, 21°C, 2563-10073 scans (~6–14 h), and no proton decoupling. Although T_1s were not measured for these samples, this delay time was estimated to be sufficient based on the ratio of P/(Fe+Mn) in the extracts (McDowell et al., 2006; Cade-Menun and Liu, 2014).

Chemical shifts of signals were determined relative to an external orthophosphoric acid standard (85%), with the orthophosphate peak standardized to 6 ppm for each sample. Signals were assigned to P compounds based on the literature (Cade-Menun et al., 2010; Turner et al., 2012; Cade-Menun, 2015) and on spiking one sample with reference compounds (α- and β-glycerophosphate) and other similar samples from another project with phytate and phosphatidylcholine, as per Cade-Menun (2015). Peak areas were calculated by integration and manual measurement on spectra processed with 2 Hz and 7 Hz line broadening, using NMR

Utility Transform Software (Acorn NMR, 2006 edition), and results were corrected for diester degradation products (Young et al., 2013; Schneider et al., 2016). Concentrations of P forms were determined by multiplying peak areas by the concentration of P extracted by NaOH-EDTA for each sample. Data from particulate samples was of sufficient quality for quantitative analysis.

4.4.4.2 Intact core leaching

A simulated leaching event was conducted to determine potential vertical movement of P as related to P application treatment. Polyvinyl chloride (PVC) cores measuring 10-cm diameter and 15-cm in length were taken from each plot at the lowEcho position site in Central Butte. Two intact cores were taken within each plot. The cores were returned to Saskatoon and frozen at -20^{o}C until analysis.

Prior to the leaching events, the frozen cores were allowed to thaw to room temperature for 24 h. Another 15-cm PVC core was then attached to the top of the soil bearing core. A water tight seal was made using parafilm and duct tape along the seam. To bring the soil up to field capacity, deionized water was gradually added to each core up to the point where it was just starting to drain and then allowed to equilibrate for 48 h. After equilibration, a 5-cm rain event was introduced to each core by adding water volume equivalent to that of a 5-cm depth in each core. Over the following 24 h, leachate from the bottom of the cores was collected and homogenized and sub-sampled for P analysis. After 48 h, another simulated rainfall event of 5-cm was conducted as described above. Sub-samples of the leachate water collected were vacuum filtered through 0.45-µm membrane filters and analyzed for P on the autoanalyzer using colorimetry.

Due to compaction during sampling, insufficient leachate water was able to be collected from a few cores for analysis and these cores were removed from the study. For statistical analysis, where applicable, values from the two cores collected from each plot were averaged.

4.4.5 Statistical analysis

Where treatments were replicated, a separation of means was conducted using Tukey's protected HSD in PROC MIXED in SAS 9.3 (SAS Institute, 2012). Assumptions of analysis were checked by using PROC UNIVARIATE to determine if the residuals data was normally distributed. Outliers were removed using Grubbs' test. More detail regarding outliers removed

can be found in the Appendix. Pearson correlations were conducted using PROC CORR in SAS 9.3 (SAS Institute, 2012).

4.5 Results

4.5.1 Spatial distribution of P

Examining the distribution of available P across the seed row in the fall after two successive seasons of P application treatments revealed some interesting aspects about the nature of the site as well as the area of enrichment resulting from different application practices. High and variable concentrations of P found in the control soil (Table 4.1) likely reflects the influence of residual fertilizer P from applications made in previous years at this site.

Table 4.1: Distribution of available P in the soil in fall 2016 in control (C) treatment as determined by modified Kelowna extraction. Units are mg P kg^{-1}.

Depth (cm)	Distance from seed row (cm)				
	10	5	0	5	10
1	27.6	25.5	26.4	22.3	29.2
4	9.6	12.1	35.7	19.5	32.1
7	6.6	6.8	12.9	8.8	13.8
10	4.1	5.6	10.1	4.0	7.5

Overall, as expected, the available P concentration was highest at the surface and decreased with depth. Some depletion in the control treatment at the depth of rooting (7-10 cm and deeper) is evident in the lower extractable P levels in the control (Table 4.1) compared to the fertilized seed placed P treatment at these depths (Table 4.2).

Table 4.2: Distribution of available P in the soil in fall 2016 in seed placed (SP) treatment as determined by modified Kelowna extraction. Units are mg P kg^{-1}.

Depth (cm)	Distance from seed row (cm)				
	10	5	0	5	10
1	19.5	17.9	18.6	20.2	21.1
4	18.8	19.9	28.0	21.1	18.5
7	18.9	15.2	19.3	15.4	13.3
10	7.0	7.1	12.3	11.2	8.1

While the seed placed P treatment showed some P enrichment (Table 4.2), the deep banded treatment showed evidence of depletion at the point of P placement deeper in the soil (Table 4.3). This may reflect better utilization of deeper placed P by the crop roots and encouragement of deeper rooting by the deep placement.

Table 4.3: Distribution of available P in the soil in fall 2016 in deep banded (DB) treatment as determined by modified Kelowna extraction. Units are mg P kg^{-1}.

Depth (cm)	Distance from seed row (cm)				
	10	5	0	5	10
1	26.2	22.6	29.0	26.7	27.0
4	25.1	23.1	13.5	17.5	25.0
7	10.4	14.3	8.1	9.3	15.1
10	7.7	6.1	5.9	7.5	9.9

The distribution of available P in the soil of the broadcast P treatment (Table 4.4) was similar to the unfertilized control treatment. While P levels at the surface were not markedly different than those of other treatments (Tables 4.1, 4.2, 4.3), possibly due to sorption, P at depth was the lowest of all.

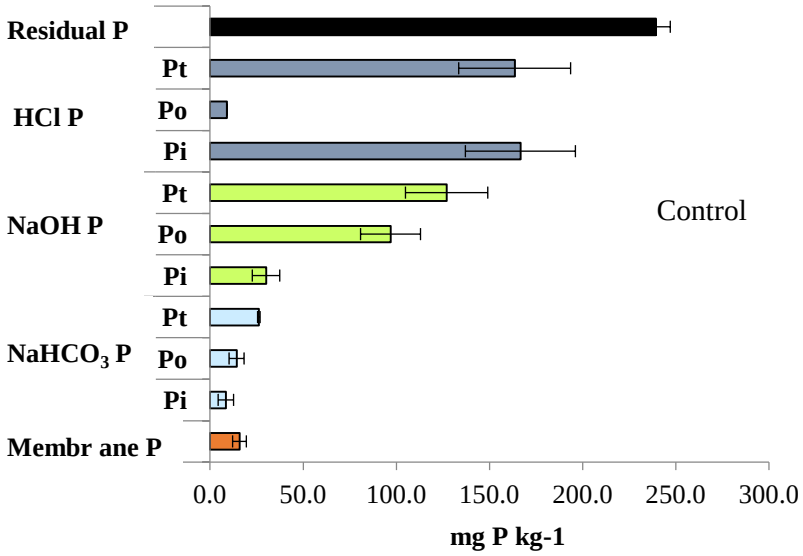
Table 4.4: Distribution of available P in the soil in fall 2016 in the broadcast (B20) treatment as determined by modified Kelowna extraction. Units are mg P kg^{-1}.

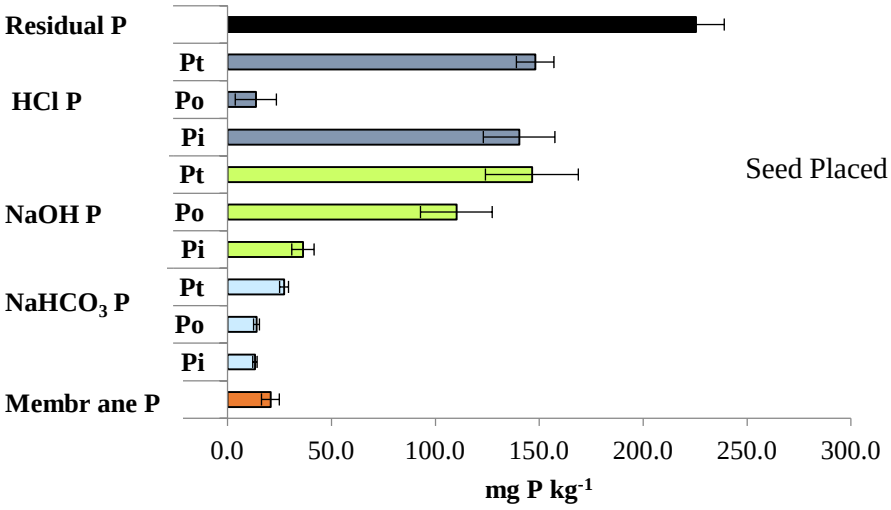
Depth (cm)	Distance from seed row (cm)				
	10	5	0	5	10
1	20.8	22.2	23.0	17.6	20.0
4	14.1	13.8	12.9	12.3	12.7
7	9.2	7.8	6.0	3.9	6.7
10	4.6	3.3	3.9	3.1	4.7

The consequence of broadcasting P without incorporation is that it may take many years for P to move through the profile and replenish P exported from depth with crop harvest. Similar extractable P concentrations in the surface 1-cm among all placement treatments at the 20 kg P_2O_5 ha^{-1} rate leads to the expectation that there will be limited differences among the placement methods at the same rate of P application in terms of P export in runoff.

4.5.2 Distribution of soil P among chemically extracted fractions

The results from the sequential extraction of soil P indicate that two years of different P application strategies had limited discernible effect on soil P forms at this site (Fig. 4.6). No significant differences were found among P fertilization treatments for the extracted pools (α=0.05). Fig. 4.6 shows similar distributions among operationally defined extractable P pools. Labile P fractions, including anion exchange membrane and sodium bicarbonate extractable P, were a small proportion of total P in all treatments, with HCl P_i (more stable calcium phosphates) and residual (recalcitrant) P dominating in these prairie soils, as reported by other researchers (Schoenau et al., 1989). Largest variability was evident in the HCl extractable P, a possible consequence of inherent variability in carbonate content within the samples.

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HCl P
Po
Pi
Pt
NaOH P
Po
Pi
Pt
NaHCO3 P
Po
Pi
Membr ane P
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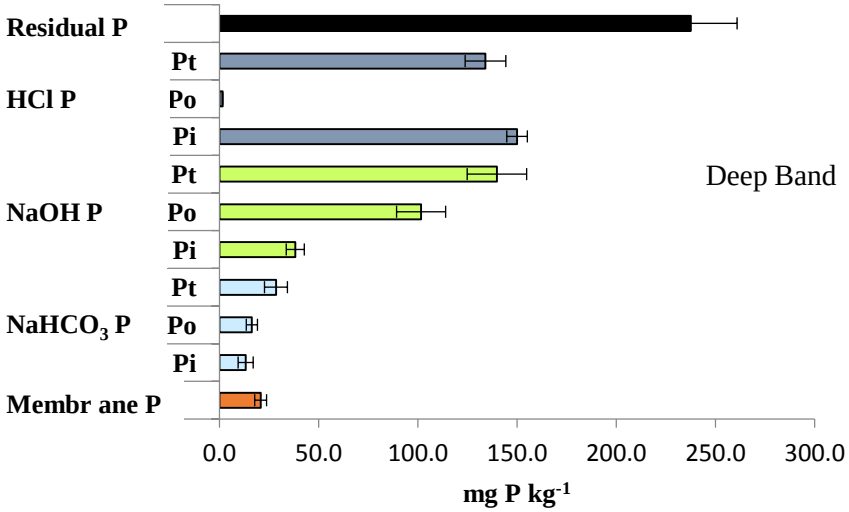
100.0
150.0
200.0
250.0
300.0
mg P kg-1
Seed Placed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HCl P
Po
Pi
Pt
NaOH P
Po
Pi
Pt
NaHCO3 P
Po
Pi
Membr ane P
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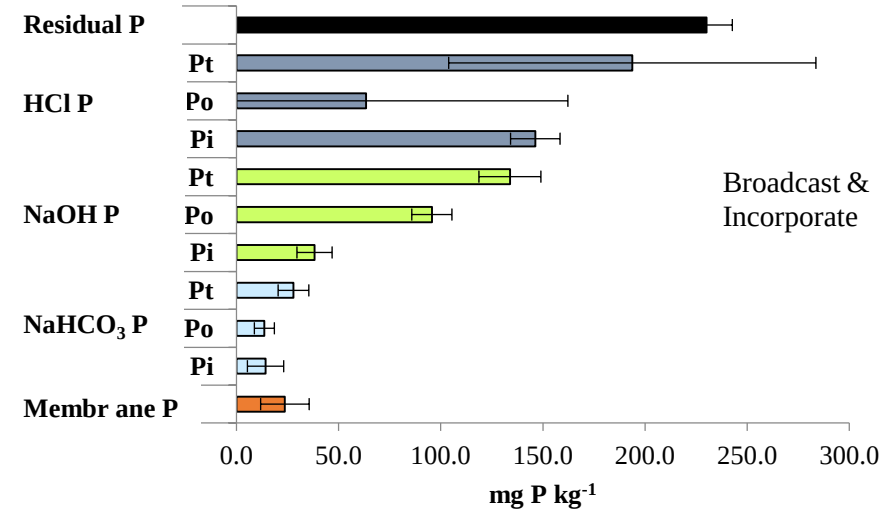
100.0
150.0
200.0
250.0
300.0
mg P kg-1
Deep Band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Po
Pi
Pt
NaOH P
Po
Pi
Pt
NaHCO3 P
Po
Pi
Membr ane P
Broadcast & Incorporate
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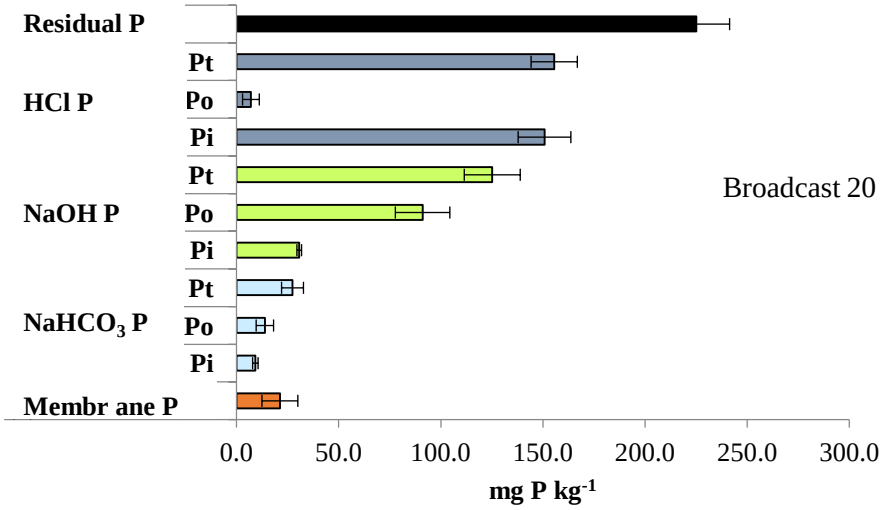
50.0
100.0
150.0
200.0
250.0
300.0
mg P kg-1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HCl P
Po
Pi
Pt
NaOH P
Po
Pi
Pt
NaHCO3 P
Po
Pi
Membr ane P
Broadcast 20
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50.0
100.0
150.0
200.0
250.0
300.0
mg P kg-1

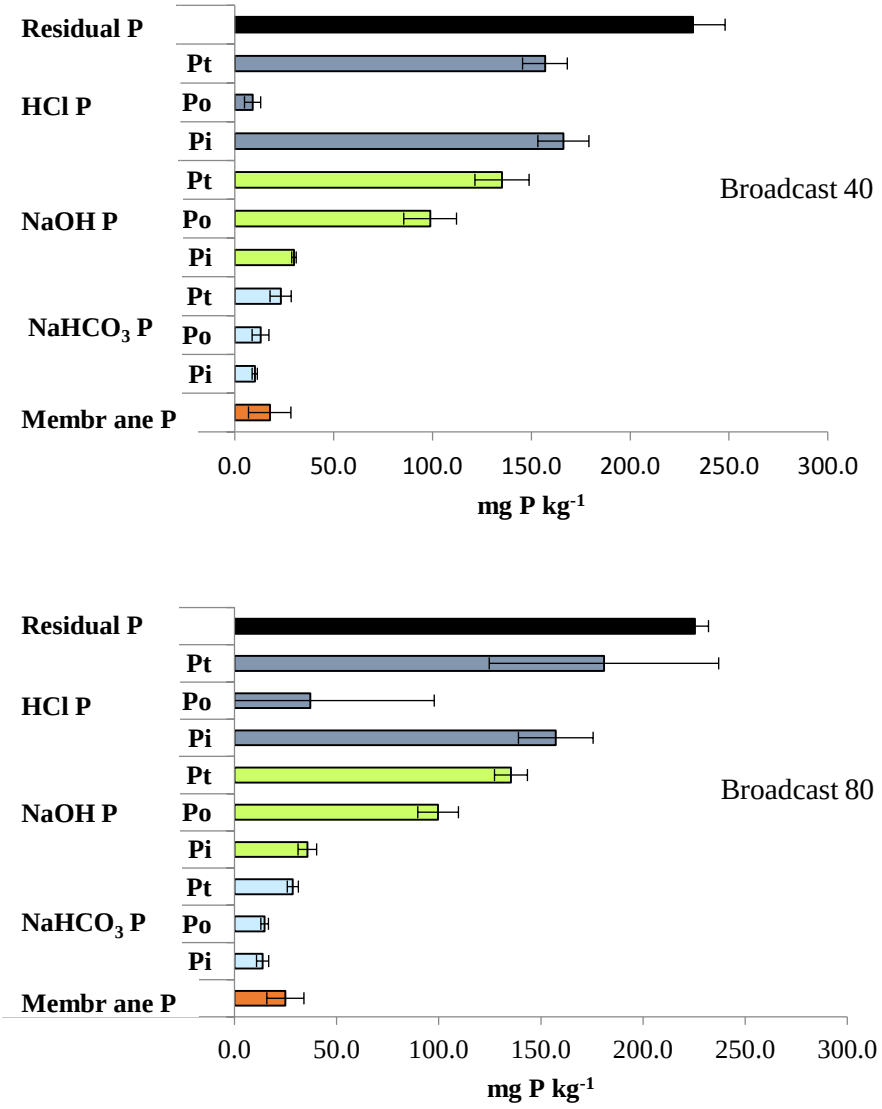

Figure 4.6: Phosphorus concentrations (mg P kg^{-1}) in sequentially extracted fractions of surface (0- to 5-cm depth) soils sampled in fall 2016 from the P fertilizer application treatments in the Haverhill site at Central Butte.

4.5.3 Snowmelt runoff

The control and P fertilization application treatments at 20 kg P_2O_5 ha^{-1} had similar amounts of P removed in runoff whereas the broadcast treatment at the high rate (80 kg P_2O_5 ha^{-1}) had considerably higher export of total P in the snowmelt runoff, along with highest concentration and proportion of P in the DRP form (Fig. 4.7).

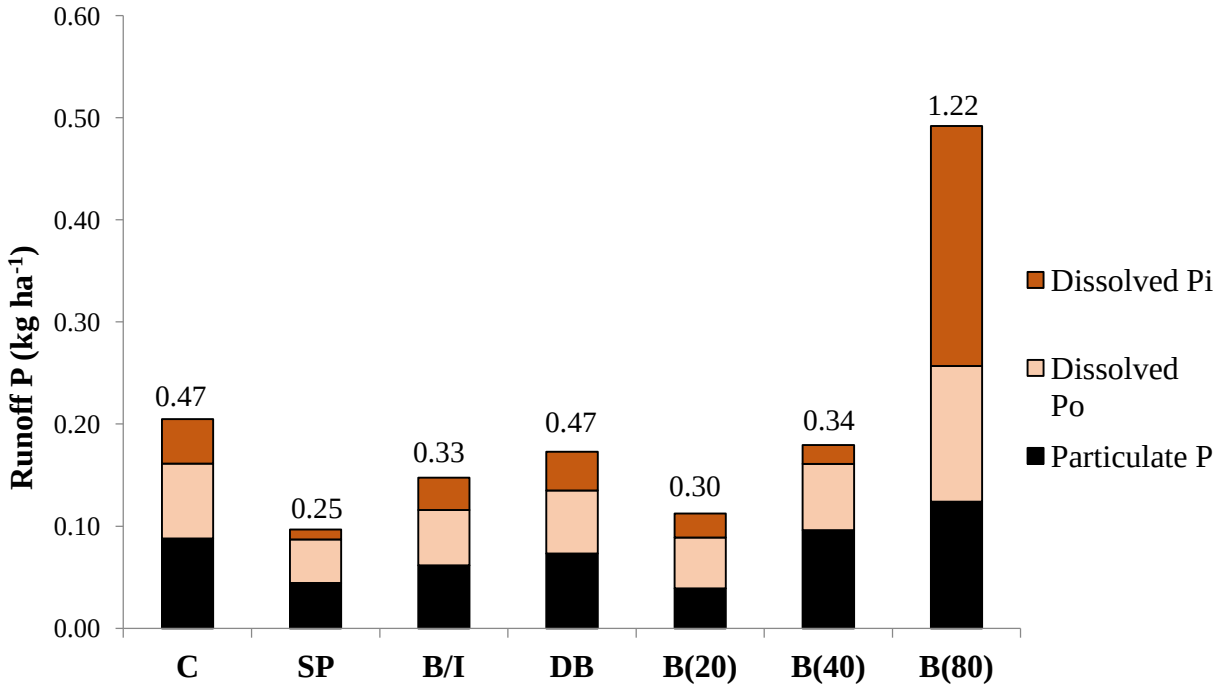

Figure 4.7: Export of P (kg P ha^{-1}) in different forms (dissolved inorganic, organic, and particulate) in simulated runoff from intact slabs removed in fall 2016 from Central Butte Haverhill site. Values above the respective bars are flow weighted water total P concentration means in mg total P L^{-1}. C, SP, DB, B/I, B denote control (no P), seed-placed, deep banded, broadcast and incorporate and broadcast respectively. Rate of P added (kg P_2O_5 ha^{-1}) in parentheses. Unless otherwise specified, the P rate for a placement treatment was 20 kg P_2O_5 ha^{-1}.

The amounts of total (dissolved plus particulate) P exported in snowmelt runoff water ranged from ~ 0.10 to 0.50 kg P ha^{-1}, with DRP comprising between less than 10% to close to 50% of total P (Fig. 4.7). These values fall in the range of values reported by King et al. (2017) of ~ 0.1 kg DRP ha^{-1} exported in simulated snowmelt water from soil slabs collected from unfertilized soil in east-central Saskatchewan to 0.5 kg DRP ha^{-1} in soils that received two annual applications of solid cattle manure. Weiseth (2015), with only one year of P fertilization treatment, had dissolved P export values that were about 10 times lower than the current study. Lack of a large difference in runoff amounts among control and low P rate fertilizer treatments is consistent with lack of large differences among treatments in P amounts at the soil surface (Tables 4.1 to 4.4) and in the distribution of P among sequentially extracted fractions (Fig. 4.6).

Results from the correlation analysis show that P fractions in runoff did not correlate with labile soil P measurements (modified Kelowna, water, and anion exchange membrane) made in surface 0- to 5-cm and 5- to 10-cm soil cores removed from the field, but did correlate positively and significantly for the extractable P in the 10- to 30-cm depths (Table 4.5). It is not clear to what extent the soil cores removed from the field represent the depths in the slabs that were used in the runoff study, but it seems likely that the slabs would include only a small portion of soil below 10-cm.

Table 4.5: Pearson correlations between P runoff fractions (Fig. 4.7) and soil labile P concentrations at three soil depths. Significant correlations (α=0.05) have been bolded. KM=Modified Kelowna, P_i=inorganic P, P_o=organic P.

Extraction	Depth		Total P	Total P_i	Total P_o	Dissolved P	Dissolved P_i	Dissolved P_o	Particulate P
	--cm--								
KM P	0-5	*r*	-0.12	-0.16	-0.08	-0.20	-0.21	-0.15	0.18
		p value	0.7652	0.6879	0.8315	0.6121	0.5791	0.7029	0.6379
	5-10	*r*	-0.21	-0.28	-0.15	-0.26	-0.26	-0.27	0.00
		p value	0.5904	0.4607	0.7066	0.4993	0.5076	0.4819	0.9973
	10-30	*r*	**0.87**	**0.91**	**0.81**	**0.87**	**0.88**	**0.85**	**0.78**
		p value	**0.0021**	**0.0006**	**0.0084**	**0.0021**	**0.0018**	**0.0039**	**0.0131**
Water P	0-5	*r*	0.09	-0.01	0.15	-0.01	-0.03	0.05	0.40
		p value	0.8264	0.9831	0.7037	0.9881	0.9425	0.8946	0.2813
	5-10	*r*	0.05	-0.01	0.10	-0.02	-0.03	0.00	0.30
		p value	0.8904	0.9813	0.8059	0.9652	0.9489	0.9925	0.4295
	10-30	*r*	**0.92**	**0.91**	**0.90**	**0.92**	**0.92**	**0.91**	**0.82**
		p value	**0.0010**	**0.0020**	**0.0027**	**0.0011**	**0.0010**	**0.0015**	**0.0127**
Membrane P	0-5	*r*	0.13	0.15	0.12	0.07	0.06	0.11	0.33
		p value	0.7324	0.7013	0.7663	0.8504	0.8815	0.7724	0.3834
	5-10	*r*	0.10	0.23	0.00	0.16	0.18	0.10	-0.12
		p value	0.8001	0.5461	0.9997	0.6843	0.6444	0.7929	0.7504
	10-30	*r*	**0.85**	**0.79**	**0.87**	**0.83**	**0.82**	**0.84**	**0.87**
		p value	**0.0030**	**0.0016**	**0.0023**	**0.0056**	**0.0064**	**0.0046**	**0.0025**

4.5.4 Intact core leaching

Amounts of DRP (kg P ha^{-1}) leached from the 0- to 10-cm depth as a result of two successive 5-cm applications of leaching water to the cores (Fig. 4.8) were more than 10 times lower than that removed in the simulated snowmelt runoff study. This reflects greater interaction of water and P with soil constituents in the simulated leaching scenario compared to surface runoff. While the amount of P leached was minimal, there were differences in vertical movement of P (Fig. 4.8) related to P application treatment. The amount of P leached in broadcast P applied at higher rates (B(40) and B(80) treatments) was significantly greater than that of the low rate (B(20)). However, no P treatments at 20 kg P_2O_5 ha^{-1} were significantly different. At the same rate of 20 kg P_2O_5 ha^{-1}, the placement of P banded below seed resulted in the greatest mean amount of P leached from the 0- to 10-cm depth. There is large variability in both the SP and B(40) treatments as evidenced by large standard deviations, such that there is no statistical difference, despite the largest difference in means among treatments. This was also shown in the P concentration, where there was no treatment effect (p=0.1690). Overall, as for lateral transport in snowmelt runoff, the downward transport of P in leaching water appeared to be more affected by rate than placement.

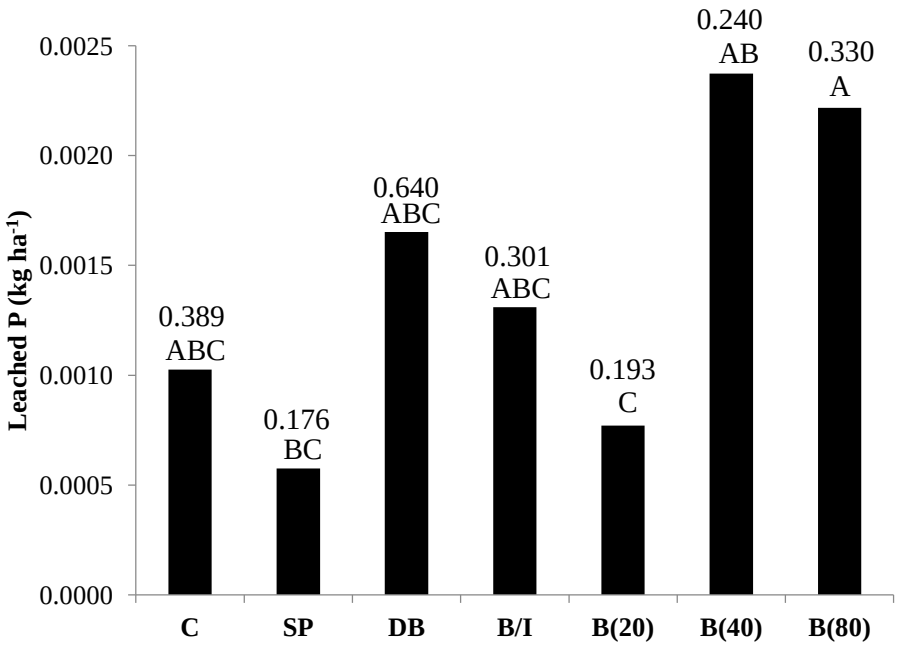

Figure 4.8: Export of dissolved inorganic P from 0- to 10-cm depth by vertical leaching of water through intact soil cores collected in fall 2016 from Central Butte P lowEcho site. Leaching event and its interaction with treatment were both not significant ($p>0.10$), but treatment was (p=0.0192). Total leached P means were separated using Tukey's HSD. Values above the respective bar are flow weighted dissolved inorganic P means in mg P L^{-1}. C, SP, DB, B/I, B denote control (no P), seed-placed, deep banded, broadcast and incorporate and broadcast respectively. Rate of P added (kg P_2O_5 ha^{-1}) in parentheses. Unless otherwise specified, the P rate for placement treatment was 20 kg P_2O_5 ha^{-1}.

Only the water extractable P was correlated with P removed in leachate and only at the lower depths (Table 4.6). Correlation was moderate in both cases and not a great proxy for predicting leached P, but appears the best tool available of those examined. As for simulated snowmelt runoff, the upper 5 cm did not appear to be useful for correlating leached P to extractable P. As P is rather immobile in soil, P at depths closer to the bottom of the core would be more important. This explains the difference between the DB and SP treatment, whose difference lies in the vertical placement of P.

Table 4.6: Pearson correlations between P exported in leachate and soil labile P concentrations at different sampling depths.

Depth (cm)		KM P	Water Extractable P	Membrane P
0-5	*r*	0.28	0.13	0.30
	p value	0.1163	0.4675	0.0950
5-10	*r*	0.22	**0.38**	0.10
	p value	0.2274	**0.0312**	0.5965
10-30	*r*	0.09	**0.57**	0.15
	p value	0.6297	**0.0007**	0.4065

4.5.5 Characterization of snowmelt P using ^{31}P NMR

The ^{31}P NMR showed compositional as well as quantitative differences in P compounds contained in the snowmelt runoff water resulting from treatment (Table 4.7). Because of the time involved and complexity of the NMR analysis, only a few samples of runoff from key P fertilization treatments were analyzed. Initially, both dissolved and particulate samples were chosen for analysis, but salt interference with the dissolved samples obstructed signal acquisition, so only one dissolved sample was of sufficient quality for quantitative NMR.

The dissolved fraction of the control sample runoff water mostly consisted of orthophosphate (Table 4.7). Dissolved organic compounds were generally low in the dissolved fraction, Of note is that the monoester:diester ratio, specifically the cM:D ratio (corrected M:D), which is higher in the dissolved fraction than the particulate fraction in the control treatment (Table 4.7). Diesters naturally exist in lower quantities in dissolved form due to lower charge densities lowering sorption competition and are also preferentially degraded through hydrolysis (Turner, 2005). Therefore, monoesters are more dominant in collected water. The monoester:diester ratio decreased in the particulate fraction of the P fertilized treatments compared to the control. Low polyphosphate levels also indicate hydrolysis. In contrast to the dissolved sample, the particulate control sample is shifted more towards a 50-50 distribution of P_i and P_o, as is the particulate fraction from the P fertilizer treatments. Interestingly,

polyphosphates are more dominant in the particulate fraction, which could indicate microbial storage of P.

Table 4.7: Phosphorus forms in snowmelt runoff water as determined by quantitative ^{31}P NMR. The upper portion of the table shows percentage composition while the lower portion of the table provides the flow weighted runoff P concentration.

Treatment[†]	Fraction	P_i	P_o	Polyphosphate	IHP	Monoester	Diester	M:D	C Monoester[‡]	C Diester	Deg	cM:D
						%----------						
Control	Dissolved	85.0	15.0	3.0	4.0	12.0	1.5	8.0	8.7	4.8	3.3	1.8
	Particulate	46.5	53.5	10.6	7.2	44.3	7.1	6.2	18.9	32.5	25.4	0.6
SP	Particulate	45.2	54.8	11.8	4.6	40.2	13.9	2.9	14.1	40.0	26.1	0.4
B(80)	Particulate	52.8	47.2	8.4	5.4	33.9	12.6	2.7	13.9	32.6	20.0	0.4
Treatment	Fraction	P_i	P_o	Polyphosphate	IHP	Monoester	Diester	M:D	C Monoester	C Diester	Deg	cM:D
						mg P L^{-1}						
Control	Dissolved	0.170	0.030	0.006	0.008	0.024	0.003	8.0	0.017	0.010	0.007	1.8
	Particulate	0.093	0.107	0.021	0.014	0.089	0.014	6.2	0.038	0.065	0.051	0.6
SP	Particulate	0.054	0.066	0.014	0.006	0.048	0.017	2.9	0.017	0.048	0.031	0.4
B(80)	Particulate	0.164	0.146	0.026	0.017	0.105	0.039	2.7	0.043	0.101	0.062	0.4

[†] Control=no added P, SP=seed placed at 20 kg P_2O_5 ha^{-1}, B(80)=broadcast at 80 kg P_2O_5 ha^{-1}

[‡] Corrected mono- and diesters, as well as the degradation coefficient and corrected mono- to diester ratio.

Monoesters and diesters were of highest concentration in the B(80) treatment (Table 4.7). This could indicate increased microbial activity and immobilization of added P by the microbial population in this treatment resulting from microbial utilization of applied P that the crops could not use. Monoesters were more abundant than diesters across all treatments examined. While diesters are less common than monoesters, this could also be a consequence of increased hydrolysis that is unavoidable in the process of sample preparation for NMR analysis. The M:D ratio was similar between the two treatments examined, but was markedly smaller than the control. However, the corrected M:D ratio was similar between all particulate samples, with the control being slightly higher. The IHP (inositol hexakisphosphate) content varied greatly among treatments, but was similar in forms present. There is not much difference in the plant derived IHP (Table 4.8). The presence of DNA and mononucleotides together with phosphatidylcholine (a phospholipid) and stereoisomers of IHP that are not plant derived (i.e. *scyllo-*, *neo-*, and *chiro-*IHP) reinforce the influence of microbes. More would be present in the B(80) treatment due to the higher amount of runoff P. It is expected that the microbial biomass P would increase after application of high rates of broadcast P fertilizer.

Table 4.8: Proportion of snowmelt runoff water P residing in different P fractions as determined by ^{31}P NMR.

Treatment†	Fraction	Ortho‡	Pyro	Poly	Phon	*myo*IHP	*chir*IHP	*neo*IHP	s*cy*IHP	g6P	α-glyc	β-glyc	Nucl	Pchol	DNA
		----------	----------	----------	----------	----------	----------	----------	**%**	----------	----------	----------	----------	----------	----------
Control	Dissolved	82.0	0.7	2.3	1.5	1.3	1.3	0.7	0.7	0.7	0.7	1.3	1.3	0.7	0.0
Control	Particulate	35.9	6.2	4.4	2.1	2.0	3.3	0.6	1.3	0.6	3.9	8.5	13.0	1.3	0.3
SP	Particulate	33.4	6.1	5.7	0.7	1.7	1.7	0.6	0.6	0.6	4.4	8.9	12.8	0.6	8.8
B(80)	Particulate	44.4	4.6	3.8	0.7	1.2	3.0	0.6	0.6	0.6	3.6	7.9	8.5	0.6	6.6

† Control=no added P, SP=seed placed at 20 kg P_2O_5 ha^{-1}, B(80)=broadcast at 80 kg P_2O_5 ha^{-1}

‡Ortho=orthophosphate, Pyro=pyrophosphate, Poly=polyphosphate, Phon=phosphonates, *myo*IHP=*myo*-inositol hexakisphosphate, *chir*IHP= *chiro*-inositol hexakisphosphate, *neo*IHP= *neo*-inositol hexakisphosphate, s*cy*IHP= *scyllo*-inositol hexakisphosphate, g6P= glucose-6 phosphate, α-glyc=α-glycerol phosphate, β-glyc= β-glycerol phosphate, Nucl=nucleotides, Pchol=phosphatidylcholine, DNA=deoxyribonucleic acid

4.6 Discussion

4.6.1 Determination of an appropriate soil test to predict P export

The ability to reliably predict P export risk through a soil assessment along with other factors like slope and tillage practice would be useful. Nash et al. (2007) examined potential for a soil test to predict P export as well as agronomic response to fertilization in Australia. The authors were inconclusive in selecting a test that was clearly superior, in part because of the variability associated with a variety of extractants. Similar challenges were encountered in the current study. Based on the results of their study, Nash et al. (2007) recommended further evaluation of the tests. Based on significant correlations obtained for both snowmelt runoff and leachate P export and the water extractable P in this study, it may be suggested that water extractable P would be the best index in these and similar prairie soils. However, emphasis may be justifiably placed on relationships to P export in snowmelt runoff in prairie soils. While leaching is an important part of P export in boreal landscapes (Palviainen et al., 2016), snowmelt runoff moved the majority of P exported in the simulations in the current study.

While all extractants provided significant correlations with snowmelt runoff P at the 10- to 30-cm depth, the water extractable P had the highest correlation coefficients. Interestingly it was the P deeper in the soil that was most closely correlated with runoff P export. The superiority of water extractable P agrees with other studies in which water extractable P consistently was among the best predictors of P export (Wang et al., 2012; Wang et al., 2010; Wright et al., 2006; Penn et al., 2006; Vadas et al., 2005; Turner et al., 2004; Schroeder et al., 2004; Kleinman et al., 2004; Torbert et al., 2002). The challenge with water extractable P is that it is not commonly used or calibrated for agronomic use in P fertilizer recommendations. In these studies, sodium bicarbonate extractable P_i (Olsen) appeared to be well suited for predicting runoff as well as being a common agronomic soil test for P. Anion exchange resin P also produced significant correlations if a threshold was surpassed (Ashjaei et al., 2010) and it also performed well in the current study. The majority of the studies reviewed in the literature looked at P export with simulated rainfall runoff and did not examine relationships with soil sample depth, with the exception of Torbert and colleagues (2002). They found better correlations with runoff P when sampling depth was reduced, taking shallower samples. Surface runoff from rainfall tends to be a more rapid process compared to a slow melt of snow on thawing soil in the spring. In snowmelt

runoff, interaction with the soil surface may dominate if the soil is frozen but when the melt occurs on thawing soil, as was the case in the simulation used in this research, there appears to be greater interaction of water with the soil at depth. For this study, only the first collection of runoff occurred when the soil was partially frozen. It would be valuable in future work to examine differences in snowmelt composition based on depth of infiltration into the soil and the correlations with soil test P, to systematically determine what samplings depths are most appropriate. Water extractable P, while a good environmental test, is quite expensive and time consuming due to requirement for vacuum filtration and challenges in obtaining a clean, particulate-free filtrate without having to filter the extract several times.

Correlations for leached P were significant, but, due to differences in quantity of exported P as previously described, may not be necessary to consider in western Canada. Water extractable P was the best available tool for predicting leachate of the three examined in this research. This may be explained by the amount of adsorbed P extracted that does not move by mass flow. Water extractable P does not extract strongly sorbed P while Kelowna extraction and anion exchange membrane may remove some sorbed P not highly susceptible to desorption and movement. Other studies (Wang et al., 2012; Wang et al., 2010; Wright et al., 2006; Penn et al., 2006; Vadas et al., 2005; Turner et al., 2004; Schroeder et al., 2004; Kleinman et al., 2004; Torbert et al., 2002) have shown better correlations between water and Olsen extractable P and mobile P than other soil tests.

4.6.2 Fate of applied fertilizer P

As the crop typically takes up at most about 50% of the applied fertilizer P in the year of application, and sometimes considerably less as observed in this study in 2015 under drought conditions, the residual P left after harvest is a potentially significant contributor to P export in fall rains and spring snowmelt runoff. Soil texture, organic matter, pH, microbial activity and soil chemical characteristics like pH are major factors influencing the mobility of P (Huffman et al., 1996). In the loamy textured, calcareous Brown Chernozem at Central Butte, there was evidence of movement of P a few cm away from where it was placed in the seed row. The spatial P distribution was influenced by the zone of root uptake, with depletion evident in the 7- to 10-cm depth. Unfortunately, the soil was not sampled deeper to look at depletion characteristics below this depth. It is unclear the extent to which sub-surface flow plays an important role in P export

in snowmelt under actual field conditions, as snowmelt slabs were only taken to approximately 10- to 12-cm depth.

In this study, export was largely affected by rate of P application, with different placement at low application (20 kg P_2O_5 ha^{-1}) rate not resulting in significant differences in runoff or leachate. Broadcast P at low rate appeared to result in relatively little elevation of labile P at the soil surface, likely due to interaction with soil P fixing constituents. Weiseth (2015) showed that inorganic mineral P was largely bound as Ca phosphates in a similar soil. Kar et al. (2012) and King et al. (2017) found in Saskatchewan soils that the applied fertilizer and manure P transforms to Ca phosphate compounds like brushite in the first few weeks.

The sequential extraction revealed, as expected, that much of the soil P resides in stable pools (Schoenau and Bettany, 1987), particularly the HCl pool that is believed to contain Ca phosphate minerals of low solubility in prairie soils (Kar et al., 2011). This study provides some evidence that these larger pools may be involved in short-term P cycling, as there was a trend for HCl P_o to be increased in broadcast application, perhaps related to microbial immobilization. However, it is difficult to draw a conclusion due to the large variability in this pool. The results from this extraction differ from those obtained by Weiseth (2015), who found a consistent 50-50 split between P_i and P_o in the HCl extractable P fraction. The HCl extractable P_i has been shown to remove Ca phosphates in the soil as apatite (Tiessen and Moir, 2008). It is unclear what the organic component of the HCl fraction represents, as it may be non-alkali extractable P_o that does have a bioavailable component (Tiessen and Moir, 2008). Furthermore, Weiseth (2015) found a reduced amount of P in the NaOH and $NaHCO_3$ fractions which appear to buffer weakly sorbed P (Kolahchi and Jalali, 2012) and represents a continuum of the same Fe and Al associated P compounds that are more and more strongly sorbed (Tiessen and Moir, 2008). The changes in these pools are most often used to illustrate the effects of differences in management over the course of many years. Differences in tillage regime could give rise to the differences in P_o observed in this study and Weiseth (2015).

4.6.3 P export in simulated snowmelt runoff and leaching water

Overall, two years of altered placement methods and application rates appear to have had limited effect on the amounts and distribution of P among sequentially extracted fractions in this soil. Fixation of added P by Ca, plant uptake, and buffering by the large stable P pools likely

limits the extent to which amounts of the labile P fractions are altered. Other researchers such as McKenzie et al. (1992) and Kar et al. (2017) have shown that several years of altered P management are required to produce detectable changes in many of these chemically separable P fractions. The observed patterns in the effect of P application treatment on the P export in simulated snowmelt runoff are similar to those found by Weiseth (2015), except for the B(20) treatment. Weiseth (2015) found that all broadcast treatments, including the low rate broadcast treatment, had elevated P export compared to in-soil placement and the control. This study had similar amounts of P exported in runoff in both the unfertilized control and all P treatments at the 20 kg P_2O_5 ha^{-1} rate. Weiseth (2015) had P export values that were considerably lower than determined here, explained by the P depleted nature of the soil used. It may be that broadcast P at low rate was more effectively used by the wheat and canola in this study than by the soybeans grown by Weiseth (2015). The excellent canola crop grown at the site in 2016 (see Chapter 3) removed considerable P from the soil. However, this study also observed that the high rate of broadcast P resulted in the highest export of P in the simulated snowmelt runoff and in the core leaching, pointing towards this practice as contributing to risk of significant P export off-site in both P deficient and sufficient soils.

As extractable P at depth significantly correlated with runoff P beyond the depth of the slab, it is unclear the extent of which sub-surface flow of snowmelt water plays in off-site export of P. During snowmelt on thawing soils, water infiltrates and moves laterally through the sub-soil as well as across the surface in runoff. In the field, such situations may be encountered in spring snowmelt where the frozen soil beneath the thawed surface acts as a barrier and promotes lateral flow. The slab runoff simulation may accentuate the contribution of sub-surface flow and interaction with soil at depth once the slab is completely thawed, but it is merely speculation at this point and is not reinforced by experimental data in this research.

Runoff P composition is reported to be affected by tillage regime (Hansen et al., 2000) and cropping system with pasture and cropland having different compositions of P in runoff, with the latter tending to have higher concentrations of DRP (Cade-Menun et al., 2013). Differences in the relative proportions of dissolved and particulate P are apparent in the literature. Some studies indicate more dissolved P in prairie systems and where snowmelt runoff dominates (Cade-Menun et al., 2013; Panuska et al., 2008; Ulen, 2003; Tiessen et al., 2010), while particulate forms dominate runoff originating from rainfall on tilled soils with limited surface residues

(Sharpley et al, 1994, 1987; Douglas et al., 1998; Lumunyon and Daniel, 2002). An important finding of this research is that application of broadcast fertilizer at the high rate of 80 kg P_2O_5 ha^{-1} increased the proportion of dissolved P_i in the runoff, which may be considered the most bioavailable. Therefore, broadcasting at high rates may be of particular concern due not only to increased potential total P load as well as shifting towards a more immediately bioavailable P form in the water.

The concentrations of total P in the snowmelt runoff and leachate collected from the cores did not exceed 1 mg L^{-1} across all treatments, with the exception of the runoff in the broadcast high P rate treatment. Glozier et al. (2006) recommends 0.26 mg total P L^{-1} as the threshold concentration for total P for a healthy water body on the Canadian Prairies. In the current study, most of the snowmelt runoff reactive P_i concentrations were near or above these concentrations. Concentrations were generally larger than those reported by Turner and Haygarth (2000), but still were within the range reported in their study (i.e. ~0.030-0.360 mg L^{-1}). Concentrations of P in the runoff were lower than in a study in Delaware, near the Chesapeake Bay, that found concentrations as high as 6.14 mg P L^{-1}, with over 40% of samples testing greater than the eutrophication standard of 0.01 mg dissolved P L^{-1} (Sallade and Sims, 1997). All samples in the current study had soluble P_i concentrations above the threshold. The snowmelt runoff collected from the B(80) treatment had the highest total and dissolved P concentration, exceeding 1 mg L^{-1} Reported ranges were even greater in a recent study by Jalali and Jalali (2017) in Iran who reported DRP concentrations in leachate as high as 8.16 mg L^{-1} and by Smith et al. (2011) measuring P concentrations in runoff from cattle overwintering sites in Saskatchewan that were as high as 12 mg dissolved inorganic P L^{-1}.

In terms of strategies for mitigating P export off-site in water in these and similar soils, reduction in P application over the course of years would result in lowered soil P status and thus should reduce P export. Soil amendments may be a short-term solution to reduce P leaching. For example, $CaCl_2$ and $CaCO_3$ have both been shown to reduce leached P in sandy soils (Yang et al., 2007; Anderson et al., 2016). Dolomite phosphate rock was also shown to reduce P leaching (Chen et al., 2006). Application of $CaCl_2$ and $CaCO_3$ could be applied pre-seeding or post harvest, but large quantities required (tonnes per hectare) would be very expensive. This is an area that may require more research for application in Saskatchewan.

4.6.4 Nature of exported P in water determined by NMR analysis

Ultimately, the concern of P export is the amount and bioavailability of the P compounds exported, which influences behavior of the P as nutrient and its promotion of undesirable biological growth in the water bodies it enters. In this study, diesters in the particulate fraction increased with P fertilization, consistent with the findings of Turner (2005). Heath (2005) indicated diesters could undergo hydrolysis, making them ultimately bioavailable, even though they are not directly taken up. Furthermore, diesters such as nucleotides that are not also present with *myo*-inositol hexakisphosphate are consistent with microbial P, as *myo*-IHP is only plant produced. As such, increased prevalence of diesters in the particulate fraction of the P fertilized treatments, especially the broadcast, could be related to greater microbial growth and P immobilization in microbial biomass induced by more available P. Other forms of IHP are poorly understood, with their origin and role unknown (Turner et al., 2012), but are thought to be microbially synthesized or altered. P uptake by this method is also not catabolically repressed. Polyphosphate is also a significant form of P in runoff, which contributes to bioavailable P through hydrolysis by microbes. Furthermore, polyphosphate can inhibit oxygen from reaching nitrogenase, increasing N fixing capacity of endophytic N fixing species, and could be an indicator for microbial growth. Perhaps the most preferred form of P in runoff is IHP, which is catabolically repressed in favor of more accessible P, in addition to being sorbed onto particulates (Turner, 2005). IHP content varied slightly among treatments with no clear pattern evident.

As noted above, changes in P composition can indicate possible changes to the microbial populations and community structure. Of considerable interest are phosphonates, a compound that is associated with anaerobic bacteria (Huang et al., 2005) that use the phosphonates as an electron source or intermediary in phosphite oxidation (Schink and Friedrick, 2000), or in N fixing bacteria as a P source (Dyhrman et al., 2009). The addition of P appeared to decrease the concentration of phosphonates in the runoff water in this study. It is possible the *scyllo*-IHP could be linked to phosphonate, but could also be natural variation. Little research has been done investigating the role and source of stereoisomers other than *myo*-IHP on bioavailability and importance in P cycling, and further work is needed to interpret the significance of phosphonates in runoff.

5. SYNTHESIS AND CONCLUSIONS

5.1 Overview

Both agronomic and environmental aspects of P fertilizer (MAP) placement were assessed in this study on a well managed, high P status, no-till soil in south-central Saskatchewan. This research provided contrast to a study by Weiseth (2015), who examined the effect of P (phosphorus) placement on an adjacent field with a history of little or no P fertilizer added, low P availability, and tillage fallow-cereal rotation. The agronomic effects, as reported in Chapter 3, were evaluated by measuring straw and grain yield, above ground P and N uptake, P yield efficiency and apparent P recovery by a wheat crop grown in 2015 and a canola crop in 2016. Yield in 2015 was restricted by drought (~1.5 – 2 T ha^{-1} wheat grain yield) and P was not limiting, such that there was no significant response of any of the agronomic variables to P fertilizer management, with only site position having a significant effect on yield. In contrast, 2016 was not limited by moisture, and yields of canola were high (4 – 5 T ha^{-1} canola grain yield). In 2016, the above ground P uptake was significantly affected by P fertilizer application strategy with the highest canola P uptake (~ 30 kg P ha^{-1}) in the high broadcast rate (80 kg P_2O_5 ha^{-1}) treatment. Canola yield was not significantly increased by P fertilizer application, indicating luxury P uptake. After harvest in the fall of 2016, higher concentrations of soil available P were observed in treatments where higher rates of P fertilizer application were made over the two years of the study, with the effects mainly observed at depths greater than 5-cm.

Overall, the agronomic results reflected the high inherent P fertility status of the soil, with further additions of P fertilizer not required to maximize yield. A comparison of in-soil and broadcast fertilizer P placement treatments revealed no differences between in-soil (seed row placed, banded, broadcast and incorporated) versus broadcasting alone on crop response. In contrast, on a similar soil type but of low P fertility, Weiseth (2015) observed a significant positive yield and P uptake response to in-soil P fertilizer placement with soybean. These findings indicate that in soils with good P fertility, P fertilizer application strategy has less impact on agronomic performance compared to a low P fertility soil where in-soil placement methods are anticipated to be superior compared to broadcasting.

Consideration of the environmental impact of P fertilizer management as related to soil P forms and mobility in runoff and leachate were considered and described in Chapter 4. Through

mapping of P distribution in soil monoliths collected in the fall after harvest, there was limited effect of placement method on available P content at the surface when applied at the low rate of 20 kg P_2O_5 ha^{-1}, but with the in-soil treatments having areas of P depletion at depth that are likely associated with zones of enhanced root growth and uptake. The separation of soil P into different chemical forms using a sequential extraction also did not show any P fertilization treatment effects based on forms and distribution among extraction pools. These findings are similar to that of Weiseth (2015) and others who have observed that alterations in P application method and rate over the short-term generally do not result in measurable differences, especially in larger stable P pools in the soil like HCl (less soluble Ca-P compounds) extractable P. Fertilizer P that is added will enter into mainly labile, but also more stable forms directly and indirectly, and the pools will buffer one another. Also, as changes in management take time to substantially shift the soil equilibrium among the different pools.

Phosphorus fertilizer application strategy influenced the amount and form of P exported from the soil in water in this study. The highest amounts of P exported (~0.5 kg P ha^{-1}) in simulated snowmelt runoff were found in the high rate (80 kg P_20_5 ha^{-1}) broadcast treatment, and the highest proportion (~50%) of the P in the runoff in the DRP (dissolved reactive P) form was in this treatment. The P removed by leaching water applied to intact soil cores (0- to 10-cm) was also highest (~0.02 kg P ha^{-1}) in the high rate treatments. The application strategy of high MAP rates applied as broadcast without incorporation would be undesirable as it would promote greater export with more highly bioavailable P in water entering into surface and sub-surface water bodies. However, at the low rate of P fertilizer application (20 kg P_20_5 ha^{-1}), there was little difference among placement method on runoff P amounts and form. This may be attributed to the high uptake of P by the high yielding canola crop and points to the importance of crop selection in reducing P export potential. Weiseth (2015) observed in his study with soybean that in-soil placement reduced P export in simulated snowmelt compared to broadcast alone, which could be explained by reduced recovery of surface placed P by the soybean compared to canola. Generally, rate appears to be more important than placement in affecting P export potential in water in these soils, but type of crop grown is likely a crucial factor that deserves further attention.

Relating the soil extraction data to P export assessment revealed that water extractable P measured at depth (i.e. greater than 5- to 10-cm) was significantly correlated with snowmelt

runoff P export (r=0.82-0.92**) and also leachate P (r=0.38-0.57*). Overall, the extractants used in this study (modified Kelowna (KM), water, and anion exchange resin membrane) were effective in predicting P runoff loss potential, as observed by other workers (e.g. Wang et al., 2012; Wang et al., 2010; Kleinman et al., 2004; Torbert et al., 2002) for correlations to runoff, with only the water-soluble P extractant having apparent predictive power for P removed in leachate from the cores. This study indicates that mobile P below the surface was making a more significant contribution to export than surface P and it is suggested further study examining increased depths be conducted to investigate this under field conditions.

Speciation of the P in the simulated snowmelt runoff water using ^{31}P NMR revealed some changes in composition, particularly an increase in organic P (P_o) in diester form with P fertilizer application that could indicate increased microbial activity for higher rates of P application. However, the shifts in P species detected in the water were small and inconclusive, similar to that observed for the chemically separable P species observed in the soil from the sequential extraction procedure.

5.2 Synthesis and recommendations

This study revealed that in a well-managed soil of high P fertility, fertilizer P application provided little benefit for crop yield in the year of application. Therefore, it is important to test for soil available P before considering P fertilizer application to determine the likelihood of achieving economic benefit in the year of application. Producers may be able to save money if P levels are high enough. However, a desire to replace P that is removed by the crop to maintain P fertility or build up levels for future crops may result in P fertilizer applications deliberately being made by producers to high P soils. Under these circumstances, low rates (~20 kg P_2O_5 ha^{-1}) applied in any manner do not appear to cause concern agronomically or environmentally, but high rates (e.g. 80 kg P_2O_5 ha^{-1}) result in luxury uptake and higher crop P removal and also greater export of DRP in runoff and leachate water. P application technique does not appear to have a great influence at low rates on these high available P soils. Soil available P levels have value both in their ability to predict crop response to P fertilizer addition and the potential off-site export of P in water. The best practice financially (i.e. no application) may also be the best environmentally in the long term to reduce excess soil P.

The need to consider and apply the four Rs of nutrient stewardship (right rate, right source, right place, right time) are reinforced by this research. While source, placement, and timing are important, the results of this research illustrate the importance of right rate in high P soils. While not having much agronomic effect, the environmental concerns of a high rate that is broadcast to provide operational efficiency are apparent in increased export with water. Therefore, it is recommended that application above previous crop export be avoided.

5.3 Future research

This research highlights gaps in investigative techniques, especially for the understanding of amounts, forms and behavior of P_o compounds in soil and water. Two of the greatest issues encountered were a result of techniques involved in the assessment of snowmelt runoff. First, there appears to be many factors influencing the export of P in the simulated snowmelt runoff. The observance of preferential contribution of sub-surface soil and therefore water flow to export of P from this experiment is of interest and needs to be validated in the field for its relative importance, as this may be an artifact of the simulation. It is recommended that future studies examining snowmelt runoff look at entire catchments with more replication as it may also address inherently high variability encountered in runoff studies. As these are labor-intensive measurements, only a few select treatments may be examined. In this case it is recommended to look at P fertilizer management practices that offer large contrast, such as in-soil banding versus broadcast alone at low and high rates, in low and high P fertility status soils. These have all been identified in this and previous studies as important aspects related to P fertilizer management. Consideration of different P fertilizer source, for example liquid P fertilizer that is soil applied or foliar, could be expanded upon in future work. A second recommendation is aimed at improving the ^{31}P NMR technique. Salt interference is a problem when concentrating water samples, as salt accumulation negatively affects detection. This limits the effectiveness of ^{31}P NMR as a tool for examining organic P, especially in prairie soils where high salt concentrations are sometimes encountered. When considering applying ^{31}P NMR in soil research, soil salt content should be an aspect before deciding on implementation, and further research should be conducted to improve the methodology for salt-affected samples.

One gap in knowledge is that while we are able to use the NMR spectra to identify various P_o compounds in soil, the role and origin of *neo*-, *chiro*-, and *scyllo*-IHP (inositol

hexakisphosphate) is poorly understood. This makes compounds such as these an important target for future research. Knowing whether these stereoisomers are microbially produced, microbially altered, or from a different source altogether, may prove useful in our understanding of P_o and cycling of P.

The role and relative important of P placement as affected by soil P status in different soils certainly becomes evident when comparing this research to Weiseth (2015). Continued investigation is required to improve inference space. It is recommended to continue to examine the agronomic response to P placement in a variety of soils with different management histories, to support the development of robust BMPs that can be adjusted and applied to many different circumstances. As the sequential extraction showed, these studies also need to be conducted over longer time periods to accurately assess P dynamics. More importantly, other soil factors that influence export, such as texture and organic matter, should also be considered, as soil tests alone are incomplete indicators of P export potential. Accounting for other soil factors in models could improve P export correlations and predictive power.

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APPENDIX

Table A1: Outliers detected in extractable P in 2015 and 2016. KM P=modified Kelowna, B(20, 40, 80)=broadcast alone at 20, 40, and 80 kg P_2O_5 ha^{-1}, B/I=broadcast and incorporated at 20 kg P_2O_5 ha^{-1}.

Year	Extractant	Site	Depth	Treatment
2015	KM P	Echo	0-15 cm	Seed placed
	Membrane	Haverhill	15-30 cm	B(20)
	Water	Haverhill	15-30 cm	Seed placed
		Echo	0-15 cm	Seed placed
			15-30 cm	Seed placed
2016	KM P	Echo	10-30 cm	B/I
				B(80)
	Membrane	Haverhill	5-10 cm	Deep band
				B(20)
		Echo	10-30 cm	Seed placed
				Deep band
				B(20)
				B(40)
	Water	Haverhill	10-30 cm	Deep band
				B/I
				B(20)
		Echo	0-5 cm	B(80)
			10-30 cm	Seed placed
				B(80)

Table A2: Outliers detected by Grubbs test in crop response in P placement trials in Central Butte, 2015. Treatments with an outlier detected are marked with an x.

Slope	Parameter	C†	SP	DB	B/I	B(20)	B(40)	B(80)
Haverhill	Grain Yield	-	-	-	-	-	-	-
	Straw Yield	-	x	-	x	-	-	-
	Above Ground N Uptake	-	-	-	-	-	-	-
	Above Ground P Uptake	-	-	-	-	-	-	-
	P Recovery	-	-	-	-	-	-	-
	P Yield Efficiency	-	-	-	x	x	-	-
Echo	Grain Yield	-	-	-	-	-	-	-
	Straw Yield	-	-	-	-	-	-	x
	Above Ground N Uptake	-	-	-	-	x	-	-
	Above Ground P Uptake	-	-	-	-	-	-	-
	P Recovery	-	x	-	-	-	-	-
	P Yield Efficiency	-	-	-	-	-	-	-

†C=control (no P), SP=seed placed, DB=deep banded, B/I=broadcast and incorporated, B(20, 40, 80)=broadcast at 20, 40, and 80 kg P_2O_5 ha^{-1} respectively. Unless otherwise specified P rate was 20 kg P_2O_5 ha^{-1}.

Table A3: Outliers detected by Grubbs test in crop response in P placement trials in Central Butte, 2016. Treatments with an outlier detected are marked with an x.

Slope	Parameter	C†	SP	DB	B/I	B(20)	B(40)	B(80)
Haverhill	Grain Yield	-	x	-	-	-	-	-
	Straw Yield	-	-	-	-	-	-	-
	Above Ground N Uptake	-	-	-	-	-	-	-
	Above Ground P Uptake	-	-	-	-	-	-	-
	P Recovery	-	-	-	-	-	-	-
	P Yield Efficiency	-	-	-	-	-	-	-
Echo	Grain Yield	-	-	-	-	-	-	x
	Straw Yield	-	-	-	-	-	-	-
	Above Ground N Uptake	-	-	-	-	-	-	-
	Above Ground P Uptake	-	-	-	-	-	-	-
	P Recovery	-	-	-	-	-	-	-
	P Yield Efficiency	-	-	-	-	-	-	-

†C=control (no P), SP=seed placed, DB=deep banded, B/I=broadcast and incorporated, B(20, 40, 80)=broadcast at 20, 40, and 80 kg P_2O_5 ha^{-1} respectively. Unless otherwise specified P rate was 20 kg P_2O_5 ha^{-1}.

Table A4: P Placement Harvest Summary in Central Butte, SK, 2015. Grain and straw yield, as well as P and N uptake, are in kg ha^{-1}. Calculation of P recovery and efficiency can be found in section 3.4.4. Means followed by the same letter within a row are not statistically different at α=0.05.

Slope	Parameter	C†	SP	DB	B/I	B(20)	B(40)	B(80)
Haverhill	Grain Yield	2227 [a]	1968 [a]	2210 [a]	1565 [a]	2396 [a]	2038 [a]	2432 [a]
	Straw Yield	1940 [a]	1540 [a]	1915 [a]	1336 [a]	2044 [a]	1647 [a]	2058 [a]
	Above Ground N Uptake	62 [a]	58 [a]	67 [a]	54 [a]	73 [a]	62 [a]	75 [a]
	Above Ground P Uptake	11 [a]	1 [a]	11 [a]	10 [a]	13 [a]	11 [a]	14 [a]
	P Recovery	-	-2.93 [a]	2.53 [a]	-5.5 [a]	11.0 [a]	0.1 [a]	3.1 [a]
	P Yield Efficiency	-	10.2 [a]	22.3 [a]	9.0 [a]	-4.2 [a]	6.8 [a]	8.4 [a]
Echo	Grain Yield	1646 [a]	1210 [a]	1667 [a]	1810 [a]	2017 [a]	1673 [a]	854 [a]
	Straw Yield	1384 [a]	1090 [a]	1384 [a]	1400 [a]	1702 [a]	1622 [a]	968 [a]
	Above Ground N Uptake	55 [a]	40 [a]	55 [a]	60 [a]	56 [a]	57 [a]	35 [a]
	Above Ground P Uptake	10 [a]	7 [a]	10 [a]	11 [a]	11 [a]	10 [a]	7 [a]
	P Recovery	-	-5.6 [a]	-1.6 [a]	4.0 [a]	6.9 [a]	-0.2 [a]	-4.4 [a]
	P Yield Efficiency	-	-22.0 [a]	1.1 [a]	8.2 [a]	18.6 [a]	0.7 [a]	-9.9 [a]

†C=control (no P), SP=seed placed, DB=deep banded, B/I=broadcast and incorporated, B(20, 40, 80)=broadcast at 20, 40, and 80 kg P_2O_5 ha^{-1} respectively. Unless otherwise specified P rate was 20 kg P_2O_5 ha^{-1}.

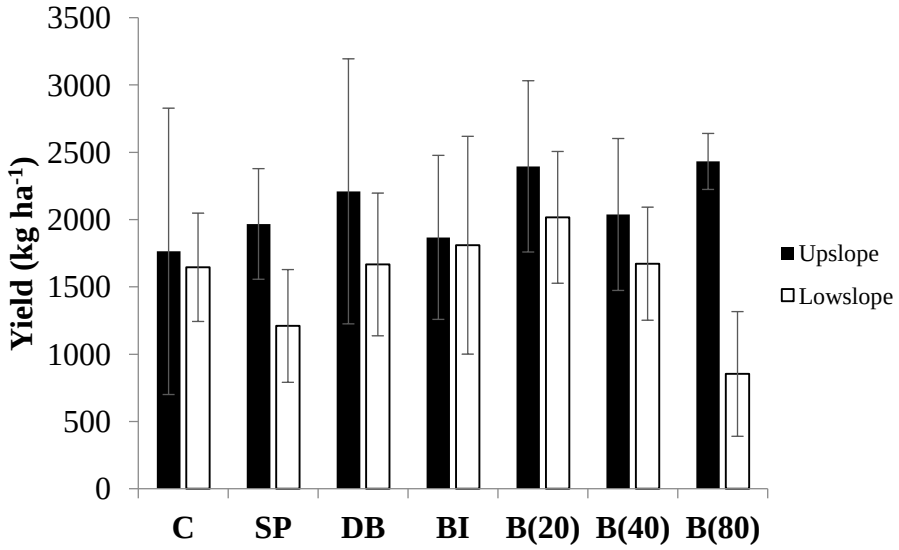

Figure A1: Wheat grain yield at P placement trials in Central Butte, 2016. Error bars are 5standard deviation. C=control (no P), SP=seed placed, DB=deep banded, B/I=broadcast and incorporated, B(20, 40, 80)=broadcast at 20, 40, and 80 kg P_2O_5 ha^{-1} respectively. Unless otherwise specified P rate was 20 kg P_2O_5 ha^{-1}.

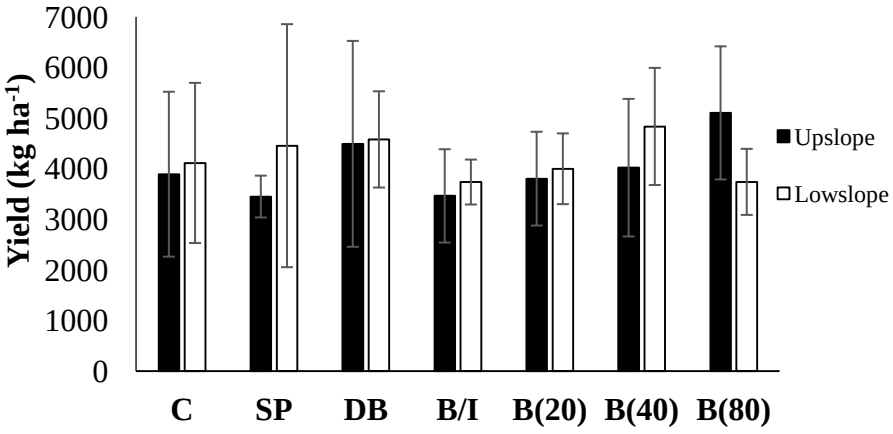

Figure A2: Canola grain yield at P placement trials in Central Butte, 2016. Error bars are standard deviation. C=control (no P), SP=seed placed, DB=deep banded, B/I=broadcast and incorporated, B(20, 40, 80)=broadcast at 20, 40, and 80 kg P_2O_5 ha^{-1} respectively. Unless otherwise specified P rate was 20 kg P_2O_5 ha^{-1}.

Table A5: *P* values for selected parameters in foliar trials in 2016. Site was not significant at α=0.05. Reported values are *p* values.

	Parameter					
Crop	Grain Yield	Straw Yield†	Above Ground P Uptake‡	Above Ground N Uptake	Grain Zn Content	Grain Fe Content‡
Canola	0.4180	0.6018	0.3340	0.3701	0.8337	0.6344
Peas	0.9248	0.9343	0.8645	0.8951	0.8568	0.9219
Wheat	0.1279	**0.0264**	0.7461	0.1459	0.2235	0.2917

†Due to residuals assumption not being met, data was power transformed
‡Due to residuals assumptions not being met, Wilcoxon scores were used to determine *P* values

In Central Butte and St. Brieux in 2016 on low soil test P fields, trials were conducted analyzing the effectiveness of foliar application on selected crop parameters outlined in Table A5. Briefly, 4 treatments containing various proportions of 20 kg P_2O_5 ha^{-1} applied as both foliar and granular seed placed MAP. Therefore, the treatments were as follows:

Control	0 kg P_2O_5 ha^{-1} seed placed	0 kg P_2O_5 ha^{-1} foliar applied
Seed Placed	20 kg P_2O_5 ha^{-1} seed placed	0 kg P_2O_5 ha^{-1} foliar applied
F25	15 kg P_2O_5 ha^{-1} seed placed	5 kg P_2O_5 ha^{-1} foliar applied
F50	10 kg P_2O_5 ha^{-1} seed placed	10 kg P_2O_5 ha^{-1} foliar applied
F100	0 kg P_2O_5 ha^{-1} seed placed	20 kg P_2O_5 ha^{-1} foliar applied

Depending on the rate of application, two concentrations of product were used. For the 5 kg P_2O_5 ha^{-1} rate, monopotassium phosphate was applied at 115 g L-1 at a water volume of 107 L ha^{-1}. For the 10 and 20 kg P_2O_5 ha^{-1} rates, monopotassium phosphate was applied at 115 and 230 g L-1 at a water volume of 107 and 214 L ha^{-1} respectively. All foliar concentrations were applied with an organosilicone surfactant Xiameter® to facilitate uptake. Products were applied at canopy closure.

Due to good growing conditions, good yields were obtained in Central Butte. Unfortunately, due to adverse conditions at St. Brieux (flooding of the peas and herbivore predation of the canola) entire crop data was lost. The only parameter significantly affected by treatment was straw yield in wheat (Table A5, A6). As no other parameter was affected, application is recommended based on ease of application rather than efficacy of placement.

Table A6: Summary of Foliar P Trials, 2016. All treatments received a P application of 20 kg P_2O_5 ha^{-1}. All units are kg ha^{-1}. Means followed by letters are separated within column and crop. Means followed by the same letter are not significantly different at α=0.05 Site was not significantly different for wheat, so comparison of treatments at both sites combined, but values are separated for convenience.

Site	Crop	Treatment[†]	Grain Yield	Straw Yield	Above Ground P Uptake	Above Ground N Uptake	Grain Zn Content	Grain Fe Content
			kg ha^{-1}					
Central Butte	Canola	C	4470 [a]	8005 [a]	23 [a]	117 [a]	0.08 [a]	0.10 [a]
		SP	3656 [a]	6739 [a]	19 [a]	91 [a]	0.08 [a]	0.07 [a]
		F25	3069 [a]	6501 [a]	16 [a]	71 [a]	0.07 [a]	0.07 [a]
		F50	4680 [a]	8867 [a]	25 [a]	118 [a]	0.09 [a]	0.09 [a]
		F100	4658 [a]	8237 [a]	24 [a]	118 [a]	0.10 [a]	0.12 [a]
	Pea	C	4976 [a]	4619 [a]	15 [a]	167 [a]	0.16 [a]	0.36 [a]
		SP	4203 [a]	3884 [a]	13 [a]	141 [a]	0.12 [a]	0.19 [a]
		F25	4468 [a]	4262 [a]	13 [a]	151 [a]	0.14 [a]	0.22 [a]
		F50	4484 [a]	4371 [a]	14 [a]	149 [a]	0.14 [a]	0.27 [a]
		F100	4709 [a]	4457 [a]	14 [a]	161 [a]	0.15 [a]	0.30 [a]
	Wheat	C	3045 [a]	3990 [b]	11 [a]	79 [a]	0.12 [a]	0.12 [a]
		SP	4580 [a]	6090 [a]	16 [a]	118 [a]	0.16 [a]	0.13 [a]
		F25	3902 [a]	5161 [ab]	14 [a]	105 [a]	0.14 [a]	0.12 [a]
		F50	4468 [a]	5607 [ab]	16 [a]	109 [a]	0.15 [a]	0.13 [a]
		F100	3170 [a]	4205 [b]	12 [a]	82 [a]	0.12 [a]	0.10 [a]
St. Brieux	Wheat	C	2422 [a]	4098 [b]	11 [a]	69 [a]	.	.
		SP	2426 [a]	5259 [a]	12 [a]	72 [a]	.	.
		F25	1702 [a]	3563 [ab]	8 [a]	50 [a]	.	.
		F50	2167 [a]	3878 [ab]	11 [a]	62 [a]	.	.
		F100	2342 [a]	4008 [b]	11 [a]	69 [a]	.	.

[†] C=Control, SP=100% Seed placed, F25= 25% foliar applied, 75% seed-placed, F50= 50% foliar applied, 50% seed-placed, F100=100% foliar applied, 0% seed-placed.